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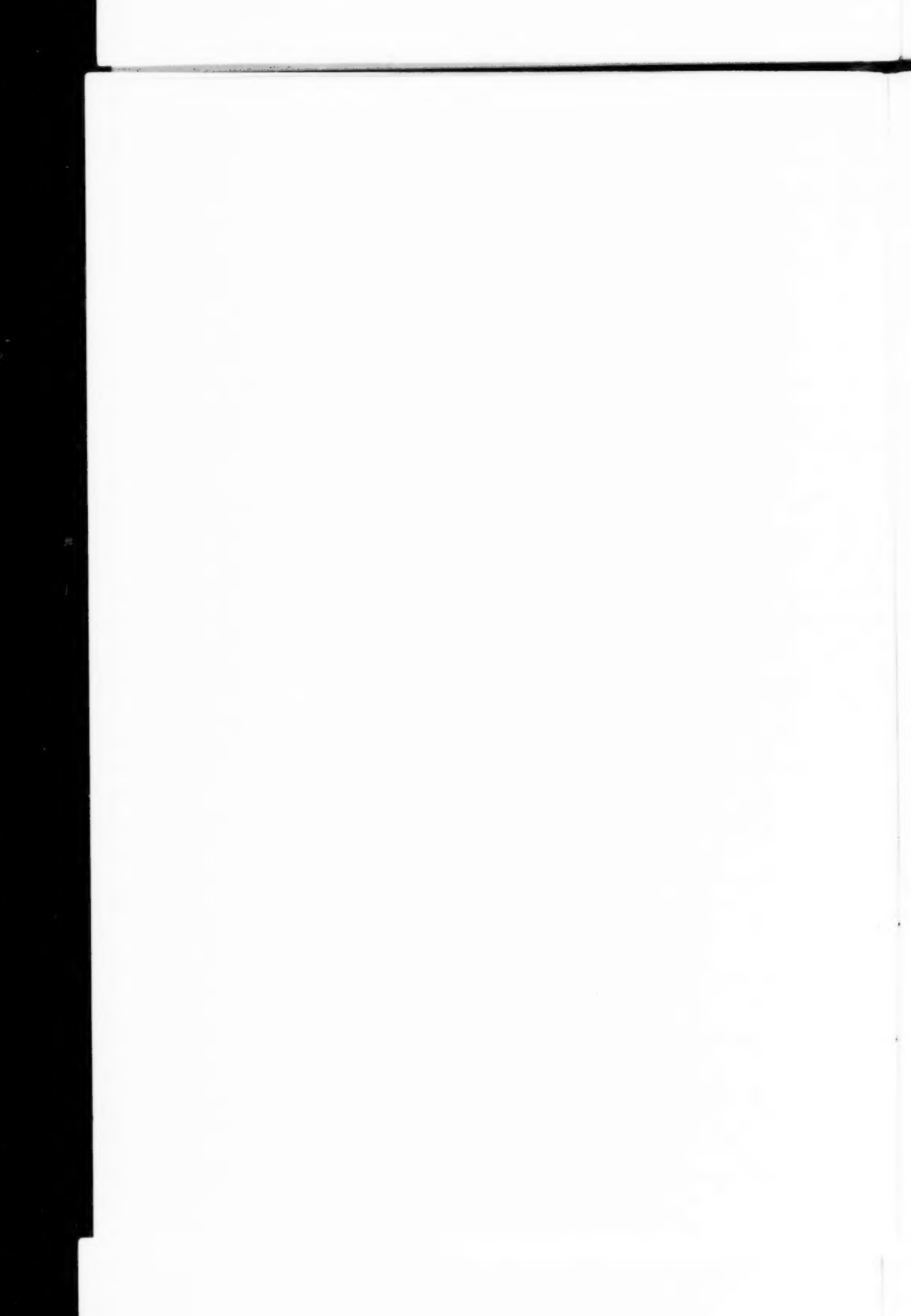
PREFACE

In this third volume of the *Annual Review of Physical Chemistry* the policies adopted for the first two volumes have been continued. Most of the subject matter has been divided according to the same broad titles which have been used in the previous reviews. However, a comparison of the details of the reviews in the three volumes will show how the emphasis has varied with the interests of the authors. Such a variation has been encouraged by the editors provided the author covered a reasonably large portion of the material which might be considered under the title assigned to him. Although this policy may result at times in rather light treatment of some topics, we believe that the reader will obtain a well-balanced survey of a field if he combines the reviews from two or three consecutive volumes.

There are a few differences between this volume and its predecessors. A review of bond distances and energies has been included because of the great interest in this subject during the last two or three years. The reviews of contact catalysis and surface chemistry and of colloids (other than high polymers) have been omitted this year but it is expected that they will be covered adequately in the next volume. However, those aspects of surface chemistry concerned with ion exchange have been covered in a review under that title.

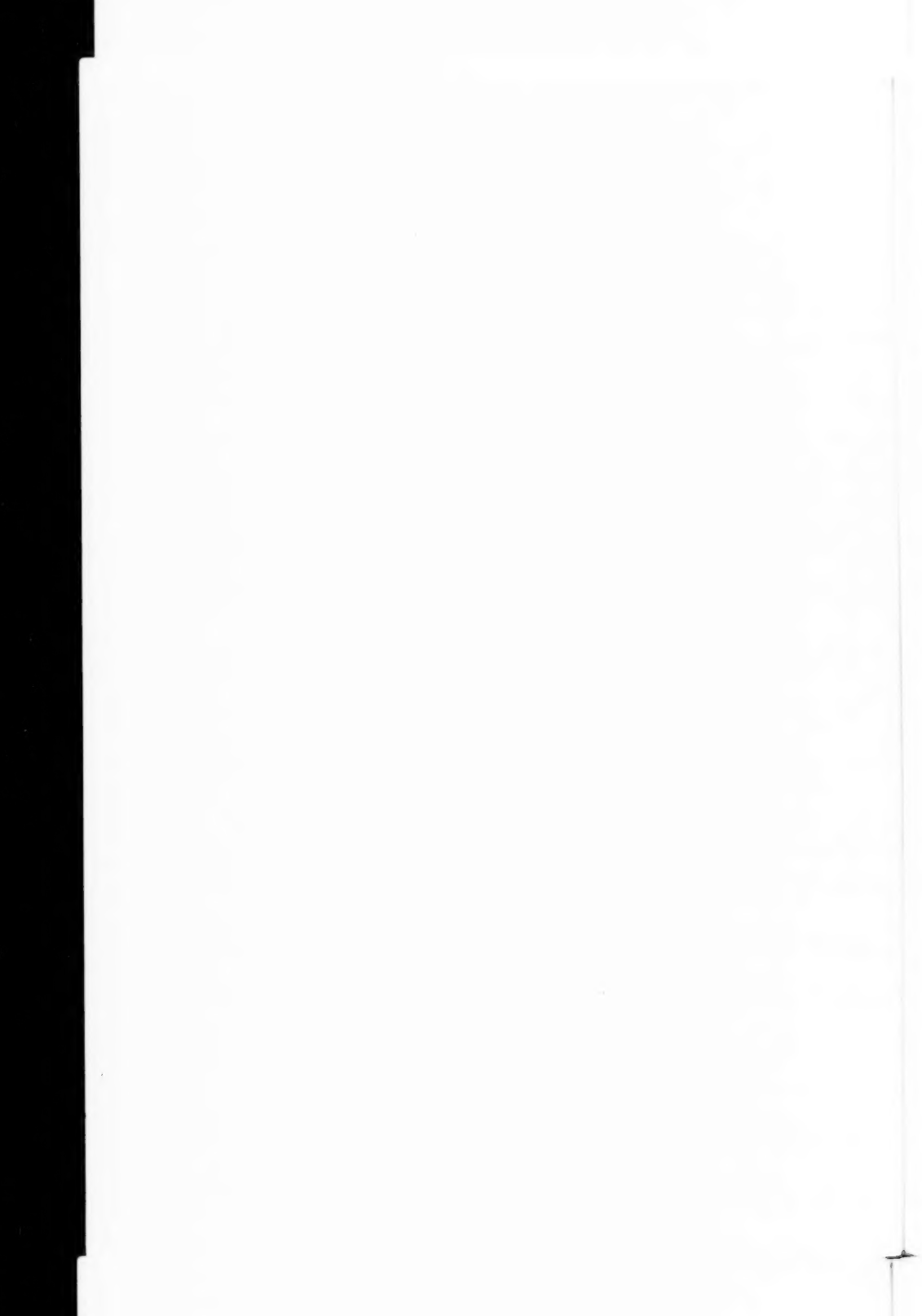
At this time we have the pleasure of giving public expression of our thanks to the authors who have co-operated in the preparation of this volume. It is only by continued co-operation of such able scientists that we can produce an up-to-date account of the developments in physical chemistry.

G.G.	J.W.W.
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W.F.L.	R.E.P.
G.K.R.	



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QUANTUM THEORY, THEORY OF MOLECULAR STRUCTURE AND VALENCE¹

BY C. A. COULSON

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This account of recent work in the theory of molecular structure and valence falls into three sections. They are: (a) What is really meant by the concept of a chemical bond? (b) What kinds of *ab initio* calculations of the energy of binding can be made, and what kind of accuracy will they possess? (c) How can we extend the discussion in the first section so that it will apply to large molecules, and particularly to the familiar resonating molecules of organic chemistry?

It will be noticed that no account is here being given of excited molecular levels, and of transitions to them; nor of any theoretical considerations which can be, and have been, adduced with much success to relate the previous descriptions of a molecule to what is conventionally called its reactivity. These latter two topics each require a separate review.

It is important to recognise that the type of answer that we shall look for under the first section is purely qualitative; that under the second must be quantitative, if it is to have any value; and that under the third will be partly qualitative and partly quantitative. For that reason such calculations are often termed "semi-empirical," since, although quantitative answers are provided by the analysis, they are nearly always obtained by an appeal to experiment at some stage in the work, in order to select the appropriate values for one or more otherwise inaccessible parameters. There is no harm in this, provided that we recognise the limitations of such an enquiry. What calculations of this sort really do is to show us that our interpretation of the particular phenomenon under discussion is the correct one by linking it with other phenomena, sometimes apparently quite distinct. In this way the theory may be said to provide us with a deeper and more fundamental understanding of our subject than would be possible by other means. We are not spared the necessity to make experiments, and to make them as carefully as we can; but we are furnished, at the end, with the satisfaction that the separate parts of chemistry all "hold together," and that the development of those concepts which give form and shape to this unity is an intellectual adventure in which both theory and experiment must cooperate.

WHAT IS MEANT BY THE CONCEPT OF A CHEMICAL BOND?

The classical answer to the question: what is a chemical bond? is provided by the work of G. N. Lewis. It is the pairing together of two electrons, having opposed spins. The work of Heitler and London in 1927 showed that

¹ The survey of the literature pertaining to this review was concluded in January, 1952.

this picture could be translated into wave-mechanical language in terms of the mutual pairing of atomic orbitals. In the early days it was supposed that these orbitals must necessarily be identical with those found in the isolated atoms. But Pauling (1) and Slater (2) showed, on grounds of symmetry, that mixtures of these pure orbitals, in the form of hybrids involving s , p , and d functions, were both possible and necessary. A good deal of attention has recently been paid to an understanding of the proportions of s , p , d in these hybrids. When the molecule is highly symmetrical, as CH_4 or SF_6 , the hybrids must evidently be equivalent, and as Hultgren (3) and others have shown, this very largely settles the matter. But with a nonsymmetrical arrangement of atoms round one central atom, symmetry alone is not sufficient to decide the combinations, and some other considerations must be introduced. The first is due to Pauling and is to the effect that the hybrids are to be chosen in such a way that their strength is a maximum. The strength is defined by the peak value of that part of the hybrid which varies with angle. With a hybrid of s and p of form $\cos \alpha \psi_s + \sin \alpha \psi_p$, which changes from pure s to pure p as α increases from 0° to 90° , the strength is $\cos \alpha + \sqrt{3} \sin \alpha$. Pauling's hypothesis (4) is that the hybrids will be such as to give maximum strength to the various bonds, always remembering the condition that all the hybrids at each atom must be orthogonal. The significance of this latter condition has been reviewed by Kimball (5) and by Coulson (6). The general argument rested upon some simplified calculations by Pauling & Sherman (7). It has recently appeared that this criterion is inadequate in detail, even though it is particularly suggestive in its general significance. Thus Maccoll (8) has shown that this theory predicts the following sequence of bond energies for various C—H bonds ethane > ethylene > acetylene, whereas the experimental values follow an inverse sequence. Furthermore, Pritchard & Skinner (9) have shown that this criterion gives false values for the energies of various 2- and 3-quantum states in H_2^+ . (Incidentally Pritchard & Skinner's work is not final [Coulson & Lester (9a)] since they did not insist on complete orthogonality between the excited state orbitals and the ground state orbitals. The importance of doing this has been stressed by Mulliken (10) who recognises that the condition of mutual orthogonality, especially when the molecular-orbital (m.o.) method is used, imposes an element of "forced hybridization" on the orbitals for the upper states.) The importance of orthogonalisation, in a rather wider context, has recently been stressed by Löwdin (11) and by Benson & Wyllie (12).

The second criterion for deciding on a choice of hybridization ratios has been developed independently by Maccoll (8) and Mulliken (13, 14). This depends on the principle of maximum overlapping. Since the exchange and resonance integrals which occur in the conventional valence-bond and m.o. theories bear a close relationship to the overlap integral, it is exceedingly plausible to suppose that the magnitude of this overlap is a good measure of the bond-forming power of the orbital. If ϕ_A and ϕ_B are the normalised atomic orbitals, usually hybrids of s , p , and d , which are involved in formation of the bond, the overlap integral is defined by

$$S = \int \phi_A \phi_B d\tau.$$

S is always less than unity. But the larger it is, the better is the hybrid adapted for bonding. It now seems likely that this criterion is the best simple one that we can apply. As Maccoll showed, it gives the correct sequence for C—H bonds of the different types mentioned earlier, and it gives reasonable values for hybrids involving both s , p , and d atomic orbitals [Craig *et al.* (14a)]. Mulliken (14) gives excellent tables for hybrids of s and p between any pair of atoms, similar or dissimilar, and at any chosen internuclear separation. There are at least two significant advantages in this measure of bond forming power. The first is that, unlike Pauling's, it does not require the radial parts of the hybridizing orbitals to be identical. This disposes of a difficulty that has often been glossed over in the past. For values of the strength of a hybrid have been quoted when the orbitals involved do not even belong to the same electronic shell of the atom. The situation represented by octahedral hybrids will serve as an example. Sometimes (e.g., SF_6) the hybrids involve ns , np , nd orbitals, but at other times (e.g., the cobaltamines) they involve $(n-1)d$, ns , np . Only in the first of these two examples would the radial parts be expected to be the same (and probably not even then!), so that a consideration of the angular part alone is clearly inadequate. In the new theory such a difficulty does not arise. Indeed (14) self-consistent-field orbitals may be used, if we wish; and it becomes possible for the relative values of S for two different hybrids to be reversed when the internuclear distance is increased, or decreased. This is, of course, one result of its greater flexibility: it has to be offset by the need to make a definite separate calculation for each case studied. Until one comes to very heavy atoms [Lester (15) has discussed hybrids for uranium, involving f orbitals as well as s , p , d], Mulliken's tables, and those of Craig *et al.*, should prove adequate. The second advantage of this measure of bonding power lies in the fact that it no longer puts such a high premium on orbitals of high angular momentum. Pauling's scheme suggests that the strengths of pure s , p , and d should be 1, $\sqrt{3}$ and $\sqrt{15}/4$. It has always seemed a little odd that d -electrons should be granted so great an ability to form bonds, since pure d -bonds do not exist, and in nearly all cases where d orbitals appear in the hybrids these occur with a smaller weight than the s or p . The new scheme disposes of this difficulty, and, as Mulliken (10) has shown, it throws a considerable light on many other problems of molecular binding. It is likely to achieve wide popularity, when qualitative and semiquantitative conclusions are being sought.

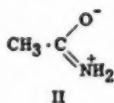
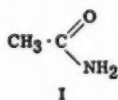
Possible hybrid types.—Of course, in both Pauling's scheme and the new one, it is extremely important to know what possible hybrids can be formed from various combinations (not necessarily involving integral numbers) of s , p , and d functions. Thanks to the work of Duffey (15a), Torkington (16), Mashima (17), Senent & Senent (18), and others, this analysis is now nearing completion. It is an essentially geometrical study, since it tells us what *can* happen; this is not necessarily the same as what does happen.

Progress here has been made along two distinct lines. On the one hand, a study of bond lengths and force constants in a related series of molecules such as $\text{CH}_n\text{X}_{4-n}$ ($\text{X} = \text{any halogen}$) has shown [Duchesne (19, 20)] that in both single and multiple bonded systems hybridization of the end atoms, as well as the central atom, is required. This has been substantiated by theoretical calculations of the dipole moment in hydrogen halide molecules HX by Robinson (21) and Kastler (22), who have shown that unless, for example, we admit hybridization of $3s$ and $3p$ in the chlorine atom, the degree of ionicity H^+Cl^- required to provide the observed dipole moment, is inordinately great. It is interesting that, as Mulliken has said: "a little hybridization goes a very long way." It is true quite generally, as Coulson (23) has shown, that without a very careful analysis of the hybridization ratios, no satisfactory account can be given of the dipole moment of any molecule in which there are lone-pair electrons. For in such cases, as Moffitt (24) pointed out, in addition to the homopolar moment caused by differences in size of the atoms of the bond, and the ionic moment caused by formal charge migration, there is a substantial term—the "atomic dipole" term, first introduced by Coulson (25)—which must be included, and which [(see 23)] may exceed all the other contributions.

The second line of progress in experimental estimation of hybridization ratios is provided by the quadrupole moment coupling constant of a molecule, referred to in Kimball's (5) review article in 1951. This constant is a measure of the dissymmetry of the electrical field at the nucleus, and may be interpreted in terms of an excess, or deficit, of p electrons relative to the isolated atom. The method has been described by Townes & Dailey (26). A recent application of this by Livingston (27) suggests that in Cl_2 , somewhat contrary to what would have been expected on the basis of our knowledge of HCl , the binding is almost pure p . Similarly the quadrupole moments of N_2 and O_2 throw light [Greenhow & Smith (28)] on the s , p percentages in the bonds. In this connection one point must be stressed, since it is often overlooked. The quadrupole coupling constant measures the total asymmetry of charge; it says nothing about the asymmetry in any one bond. The situation is similar to that with bond energies. Total heats of formation tell us nothing directly about the energies of the separate bonds. But just as it has been possible to devise tables of bond energies, and to use them most profitably, there seems no reason to doubt that before very long much the same will be true about the hybridization ratios in different bonds. There is hardly enough evidence, yet, however, to start generalising. A list of a good many results, with their relation to ionicity, has been given by Gordy (29).

Ionic character.—It should be obvious from the above account that the concept of hybridization now dominates all discussion of molecular structure. One result has been a diminution of interest in the older theory of covalent-ionic resonance. Indeed, once it is recognised that a hybrid atomic orbital does not possess a centre of symmetry, as the pure s , p orbitals do, then it follows that the centre of position of the electron cloud of the orbital is separated from the corresponding positive charge on the nucleus. Thus it

is clear that whenever there is hybridization, there will be an atomic-dipole and we can no longer use the total dipole moment for a bond to infer the relative weights of covalent and ionic parts. As Moffitt and also Coulson, Danielsson & Greenwood (29a) have shown, the "intrinsic" ionicity of bonds such as N—H, O—H, and F—H is considerably less than the formal ionicity calculated by use of conventional resonance theory. A full account of the present situation has been given by the writer (23), in a paper read at an important conference organised by the Royal Society in London. At the same conference Cottrell & Sutton (30) provided far more detailed information than was previously available concerning the way in which an ionic component in a covalent ionic wave function could take care of differences in electronegativity of the atoms. Despite its dwindling theoretical status, this theory still remains a most valuable and, within limits, reliable form of calculus, and is able to "interpret" and to predict bond length changes and other properties of homologous series. A full account of these successes is given in another paper read at this conference by Warhurst (31), to whom many of the more recent developments are due. At the moment of writing there seems to be a partial abhorrence among many chemists of the notion of covalent-ionic resonance. This is probably one result of an overemphasis in the past. It is becoming clear that ionic structures are less essential than we had once supposed. For example, it used to be argued that in the acid amides, in addition to the normal covalent structure such as I we require ionic structures such as II. At one time Pauling suggested something like 20 kcal./mole resonance energy of this kind. But Bates & Hobbs (32) have now shown that in this (and other) cases the observed dipole moment can practically be explained by simple addition of revised bond moments. In I the observed moment is 3.4 D., the calculated moment is 3.1 D.



This does not leave much to be provided by II. A similar situation arises in the carboxylic acids. It is too early yet to say that chemistry books of the future will have to be rewritten in terms not invoking the concept of resonance. Indeed the present writer believes that this will not occur. But it is pretty clear that the emphasis will be much less than in the last two decades.

Electron-correlation.—Hybridization has now been shown to be intimately involved in bond energies, bond lengths, bond angles, and in bond strain [Coulson & Moffitt (33)]. But it is by no means the only important factor. One of the additional factors has recently been discussed in some detail. It is the electron-correlation within the bond. The concept is best described in relation to the molecular-orbital method. Let us consider the ground state ($\sigma 1s$)² of H₂. Then, if ϕ_a and ϕ_b are atomic 1s orbitals, the occupied m.o. is $\psi = \phi_a + \phi_b$, and the m.o. description of the ground state is provided by the wave function $\Psi = \psi(1)\psi(2)$. One large objection to this is that it does not

take sufficient account of the electron-electron repulsion, which will tend to keep the two electrons at opposite ends of the bond. A conceptually simple way of introducing this would be to multiply Ψ by a term which is small unless r_{12} (the distance between the electrons) is large. It is interesting to recall that James & Coolidge (34), in their monumental attack on this molecule, found very severe limits to the calculated dissociation energy (4.27 ev instead of 4.73 ev) unless they incorporated some r_{12} -terms in their wave function. But now Frost & Braunstein (35), extending some earlier exploratory work of Frost, Braunstein & Schwemer (36), have shown that if the extra factor $(1 + pr_{12})$ is introduced in Ψ , a considerable improvement is possible. The importance of the r_{12} dependence is shown that in the equilibrium configuration the numerical value of p is 0.28, in atomic units. (A term of this general type was fifth largest in the 13-term wave function of James & Coolidge.) The final energy, while still worse than James & Coolidge's value, is no less than 0.5 ev better than the best-possible pure m.o. energy obtained some years ago by the writer (37). It is well recognised that in two- and three-electron atomic spectra [Huang (38); Majumdar & Chowdhury (39); and Thaler (40)] no proper account can be given of the behaviour of two electrons with opposed spins, but otherwise in the same space orbital, without introducing r_{12} -terms into the wave function. It is not surprising that the same is true in molecules. Some reasons for this have been given by Lennard-Jones & Pople (46). If, in the case of the hydrogen molecule, the r_{12} -term in the Hamiltonian were completely absent, there would be a rigorous quantisation of the angular momentum of each electron around the internuclear axis. The presence of the r_{12} -term, by trying to force the electrons as far away from each other as possible, introduces a correlation in the angular coordinates, and thereby breaks down the two separate quantisations. There still remains the total angular momentum around the axis of symmetry, which gives the Σ , Π , Δ , \dots character to the various molecular states. But it may be supposed that the separate σ, π , \dots character of each electron is partly destroyed, and mixing occurs. We ought therefore to regard the ground state Σ as built up by superposition of elements in which the electrons occupy orbitals $\sigma\sigma, \pi_+\pi_-, \delta_+\delta_-, \dots$, where, for example, π_+ and π_- denote molecular orbitals of unit angular momentum around the axis, and with positive and negative direction respectively. The chief failure of a normal m.o. description is that, at best, it can employ $\sigma\sigma$ elements. A simple calculation using wave functions and integrals attributed to Hirschfelder & Linnett (42) shows that a distinct advantage exists by using just $\sigma\sigma$ and $\pi_+\pi_-$ elements, a conclusion already reached some years earlier by Nagamiya (43). However, the full factor $1 + pr_{12}$ is much better. It is a great pity that the complexity of the resulting integrals makes it rather unlikely that the method will be of much use in polyatomic systems. Its value is chiefly qualitative, in showing that although electrons with opposed spin may occupy the same orbital, they continue to exert very considerable repulsions on each other which will provide a significant degree of correlation between their instantaneous positions in these orbitals.

Status of hybridization.—It has generally been supposed that the basis of directional valency lies in the concept of hybridization. It is this conviction which has inspired most of the work reported above. The reasons for this belief are interesting and worth trying to survey. In their simplest form they are (a) inability of pure s , p orbitals to give correct angles in, for example, methane; (b) greater bonding power of a hybrid as compared with a pure s , $p \cdots$ orbital; (c) reduced repulsive forces between electrons in different bonds. It is quite clear that no adequate account of a molecule like methane can be given, which will preserve the idea of four distinct and equivalent bonds unless we are allowed to replace the spectroscopic s and three p orbitals of the valence shell of carbon by four hybrids. It is only when we have done this that the tetrahedral character of a carbon atom becomes apparent. We might almost say that the facts of experimental chemistry force this concept upon us. But when we have once permitted hybridization, we obtain new atomic orbitals whose associated charge-clouds are markedly directional. As we said earlier in this account, such orbitals are well-adapted to form strong bonds because of their great power of overlapping. However, the same directional character which makes for strong bonding equally well reduces intra-atomic repulsions. For if, in carbon, we "prepare" the atom in such a way that its four valence electrons occupy orbitals which project in the required tetrahedral directions, it follows that the electrons in these new orbitals are, on the average, further removed from each other than they were in the unprepared atom. Thus the asymmetry of charge distribution induced by hybridization results in a reduction in the Coulomb repulsive forces which always exist between electrons, and which, as Van Vleck and others showed many years ago [e.g., Van Vleck (44, 45)] are extremely important in deciding valence angles.

A striking numerical example of this reduced repulsion has recently been provided by Lennard-Jones & Pople (46). These authors evaluated the simple electrostatic repulsion that exists (a) between the $2s$ and $2p$ electrons in beryllium $(1s)^2(2s)(2p)$ and (b) between the same electrons when they occupy the equivalent digonal hybrids $s \pm p$. The reduction which they found was from 0.18 to 0.14, in suitable units. Since the sum of the Coulomb and exchange energies is only 0.14, the reduction amounts to about one-quarter of the whole. In the same way the exchange integral will be reduced by hybridization. Further, since the exchange integral dies away with distance more rapidly than the Coulomb integral (exponential rather than inverse power law of variation) we may also anticipate that hybridization reduces the extent of exchange between electrons in different bonds. This is found to be the case. In beryllium, which is a rather extreme example, the reduction as between (a) and (b) above is from 0.040 to 0.004, in the same units. Reduced exchange of electrons between one bond and another implies a greater degree of pairing within the bonds. Now the idea of a chemical bond has always been recognised as depending on the pairing of the electrons involved. Thus hybridization is once more seen to be a foundation element in any description of a chemical bond in a polyatomic molecule. It is only when we

use this concept that we are able to maintain the concept of a bond in its simplest form.

Directional properties within an atom.—In view of this it is extremely interesting to notice that a quite different approach has recently been made to the question of valence angles. In this new approach no mention is made of hybridization, but a more careful study is made of the relative positions of the valence electrons in the isolated atom. For this purpose it is not necessary to "prepare" the atom by any form of hybridization. All that is necessary is that the valence electrons must be put in orbitals, which may be genuine spectroscopic orbitals, in such a way that there are as many unpaired electrons as the valence number of the atom. Thus carbon, in its normal tetravalent condition, would be discussed as if it were in the sp^3 state (effectively a 5S state) and not the valence state (44, 45) of Van Vleck, Mulliken (47), and Moffitt (24) which is based on tetrahedral or related hybrids of the s and three p orbitals. And beryllium would not be in its ground (zerovalent) state $(1s)^2(2s)^2$ but in the excited (divalent) state $(1s)^2(2s)(2p)$ as discussed by Lennard-Jones & Pople.

The calculations which we are now reporting attempt to answer the following question: given that the atomic wave function is that function appropriate to the known valence number, and that therefore we know its approximate form and the corresponding electronic distribution, what are the most probable relative positions of the electrons, both valence and non-valence? The surprising answer is that their centres of position for maximum probability are nearly always such as to suggest the observed valence angles. The original idea of a discussion of this kind seems to have originated with Artmann (48), but it has been "rediscovered" by Zimmerman & Van Rysselberghe (49) and developed further by Linnett & Poë (50). Before describing a particular example to illustrate this idea, it is necessary to stress that what is being discussed is not the probability distribution for one electron (which may be in any sort of orbital, according to the manner in which we manipulate the determinantal wave function), nor is it the mutual probability distribution of two electrons. It is the complete system of atomic electrons with which we are dealing; and we ask what are the mutual relationships between the positions of all these electrons, which we should be most likely to find. This is equivalent to saying that if $\psi(r_1, r_2, \dots, r_n)$ is the wave function for the n electrons, we require the mutual values of r_1, r_2, \dots, r_n which will make $\psi\psi^*$ as large as possible. Sometimes this analysis can be completed analytically; but often it has to be achieved by numerical methods.

First, let us consider beryllium in the excited state $(1s)^2(2s)(2p)$ already referred to in a different connection. Linnett & Poë show that the situation of maximum probability occurs when two electrons are at the nucleus, and two others are at a distance $1.64 a_0$ from the nucleus, in exactly opposed directions. Now in this, no mention occurs of specific orbitals, and hybridization is not so much as hinted at. But this most probable arrangement of the electrons suggests two inner electrons with no bonding power, and two

others "ready" to form bonds in the linear form such as was previously assigned to the working of digonal hybridization.

Next, consider boron. In its trivalent state $(1s)^2(2s)(2p_x)(2p_y)$ the most probable arrangement is one in which two electrons are at the nucleus, and the other three at the corners of an equilateral triangle surrounding the nucleus. This is most suggestive in view of the known fact that boron, in compounds like $B(CH_3)_3$ and BCl_3 , exerts its valencies in plane trigonal directions.

Similarly in sp^3 carbon we find the most probable arrangement is one in which two electrons are at the nucleus and the other four are tetrahedrally placed around the nucleus. It is almost as if the electrons, in trying to repel one another and satisfy the Pauli Exclusion Principle, were forcing themselves into positions suitable for bond formation, such as is observed. Sometimes the agreement is astonishing. In nitrogen, the angles between the three odd electrons are found to be 108° , which is exceedingly close to the 107° between the NH bonds in ammonia. In fluorine, the angle between the odd electron (later to be responsible for a bond) and the pairs of close electrons is 101° . This is certainly rather less than the angle between the FH groups in polymeric $\dots HF \dots HF \dots HF \dots$, which electron diffraction has shown to be about 140° . But at least it provides some sort of explanation of the directional character of the hydrogen bonds from fluorine. Previously there was none which could be said to be satisfactory.

Role of nonbonding electrons.—This discussion leads us naturally into a consideration of the role of nonbonding electrons. If these are in the valence shell, they are often referred to as lone-pair electrons. Thus in NH_3 there is one lone-pair and in H_2O there are two lone-pairs. It appears from recent work that the influence of these lone-pair electrons on valence angles is much greater than used to be supposed. Several lines of evidence seem to lead to this conclusion. Returning for a moment to the work of Artmann which has just been described (48), it was there shown that in N, if we consider only the three $2p$ orbits, and pay no attention to the nonbonding electrons (here supposed to occupy the $2s$ orbital) the most probable positions of the electrons would be when their directions to the nucleus make angles of 90° with each other. This is a transcription of the familiar argument about 90° valence angles in p - p bonding. But Linnett & Poë (50) showed that when the other electrons, and particularly the lone-pair electrons, were included, the valence-angle opened out to 107° . This makes it clear that the lone-pair electrons strongly influence valence angles. In this situation the converse is also true, that the lone-pair electrons have their orbits changed as a result of bond formation. This conclusion could have been predicted by use of the principle of maximum overlapping. If the observed HNH angle in ammonia is 108° , the bonds make an angle which is close to the tetrahedral angle, such as is found in methane ($109^\circ 28'$). It follows that the hybrids at the N atom must be approximately tetrahedral also. Now if three of these hybrids make a tetrahedral angle with each other, it can easily be shown [Coulson (6)]

that the fourth must also be tetrahedral. Consequently the lone-pair electrons in NH_3 occupy an orbital rather strongly directed away from the N atom on the opposite side to the three hydrogens. This explains their influence in determining the shape of the molecule, because if these electrons do not have a centre of position at the nucleus, they will exert powerful Coulomb forces, of a nonradial character, on the other electrons. The directional character of these is now seen to be quite natural.

The first explicit recognition of this seems to be due to Mulliken (51), though the most complete early attempts at actual calculation are those of the present writer (52). During the last two or three years, however, Lennard-Jones and his students [(53) and later papers] have extended this work and confirmed the earlier conclusions in almost every respect. The general argument is sufficiently simple to be presented without the aid of any large amount of mathematics. A longer review of this work is provided by Lennard-Jones & Pople (54), and Lennard-Jones & Hall (55).

If we adopt the m.o. approach, then the electrons in a molecule are allotted to certain definite orbitals. A description of the molecular state consists in an enumeration of the possible orbitals and a statement about how many electrons there are in each, and with what spin. The Pauli principle, of course, is accepted. In general, and particularly if these orbitals are calculated by the self-consistent-field method associated with the name of Fock, they will extend over the whole molecule, and are therefore described as delocalised. In approximate calculations of these m.o.'s they are usually regarded as if they could be built up out of suitable atomic orbitals of the constituent atoms. Such an assumption may be convenient, but it is by no means necessary. Let us suppose that these m.o.'s have been obtained, and they can be represented as ϕ_1, ϕ_2, \dots . In the ground state of the molecule, with an even number ($2n$) of electrons these will occupy the lowest n levels, and the wave function will be a determinant of $2n$ rows and columns. This determinant can be summarised by its leading diagonal, and if we use the convention that a bar denotes spin β , and the absence of a bar denotes spin α , this determinant is

$$\psi = \det \{ \phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) \dots \phi_n(2n)\bar{\phi}_n(2n) \}. \quad 1.$$

If we are concerned with the molecule as a whole, this is all that we need to say. But quite clearly a wave function like the one above says nothing about a bond, in the sense in which a chemist is familiar with it, possessing characteristic bond length, force constant, dipole moment, etc. However, as the writer showed (52), the determinant may be manipulated in ways familiar to mathematicians, without in any sense altering its value, when expanded in full. One type of manipulation is the addition and subtraction of rows or columns. More generally the individual orbitals ϕ_1, \dots may be replaced by any new set $\theta_1, \theta_2, \dots$ derived from them as linear combinations of the form

$$\theta_1 = \sum_{s=1}^n c_{1s}\phi_s,$$

provided that certain simple restrictions are applied to the c 's. These are that the matrix of the c 's, $|c_{rs}|$, is orthogonal. (If the coefficients c_{rs} are allowed complex values, the matrix must be unitary.) In this way we have an entirely equivalent expression to equation 1, of the form

$$\psi = \det \{ \theta_1(1)\bar{\theta}_1(2)\theta_2(3)\bar{\theta}_2(4) \dots \theta_n(2n)\bar{\theta}_n(2n) \}, \quad 2.$$

Now it may be possible to choose the matrix of the c 's in such a way that each individual θ function (say θ_r) is effectively localised in a particular region of space, such as between two atoms A and B. In that case we could say that two electrons in θ_r represent the bond A—B. The condition that there shall be characteristic bond properties is now seen to be that it shall be possible to convert equation 1 into equation 2 and have each θ_r more or less localised. As the writer showed some years ago for the particular case of methane (56) this can be done, and provides a reasonable value for the dipole moment of the C—H bond. Often, as suggested by Lennard-Jones, it may be better to start with equation 2 and so work round to equation 1. This is particularly true if we are interested in ionisation potentials, for as was shown by Fock and others about 1930, the ionisation potential of an electron is almost equal to the binding energy of the electron calculated as a one-electron problem. The proof is entirely similar for atoms, molecules, or crystals. Calculations of this kind have been made for the paraffin series by Hall (55, 57) and give excellent agreement with experimental ionisation potentials found by electron impact, for molecules from propane to decane.

It is important to realise that neither equation 1 nor equation 2 is "more correct" than the other. They are different ways of expressing the same wave function. If we are interested in the molecule as a whole, as for example its total energy or its spectral properties, then equation 1 which involves delocalised m.o.'s is almost certainly the more appropriate. But if we are interested in the molecule as composed of bonds, then equation 2 is to be preferred. We might, in a rather loose kind of way, refer to equation 1 as the physicist's and equation 2 as the chemist's description of a molecule. It is only when conjugated single and double bonds occur, as in benzene, that the change from delocalised equation 1 to localised equation 2 turns out to be impossible. It has been recognised by chemists since about 1865 that no ordinary bond diagram could be used for molecules of this kind. Kekulé's "dynamic oscillation" is now translated into wave-mechanical terms as the impossibility of localising the valence electrons in the region of separate bonds.

One interesting corollary is involved in the localisation represented by equation 2. If some of the new m.o.'s θ_r correspond to bonds, the others correspond to nonbonding orbitals. But now, on account of the need for them to be orthogonal to all the other θ functions, they are no longer pure s or pure p orbitals, but are "pushed away" from the nucleus, just as if they were strongly polarised by the other electrons present. If we tried to express the orbitals of these nonbonding electrons in terms of s and p functions we should be obliged to use hybrids; in this way we return once again to the descrip-

tion already obtained earlier in this account. The interaction between the nonbonding electrons and the electrons of the bonds is considerable, and plays a large part in determining valence angles. It has been discussed in terms of the various energy contributions for the case of H_2O by Lennard-Jones & Pople (46). For analogous reasons the interaction between pairs of water molecules, including the hydrogen bond, is closely associated with the directional character of these lone-pair electrons (58).

Configuration interaction.—We have just seen that the idea of a chemical bond is represented by the existence of a pair of electrons with opposed spins in a localised orbital θ . Until now we have usually supposed that both electrons have occupied the same molecular orbital. Clearly this is inadequate as a description, because the electrons in the bond will exert considerable Coulomb repulsions on each other. One result of this is that as we mentioned earlier, there will be a degree of correlation between their positions, so that they keep as far away from each other as possible. We have already referred (34, 35, 36) to one way of allowing for this, by the introduction of a factor such as $(1 + pr_{12})$ into the wave function. Another way, which has recently been attracting considerable attention, is to use a sum of two or more determinants instead of only one. We can illustrate this best by a discussion of the simplest case, recently studied by Coulson & Fischer (59) for the molecule H_2 .

If we confine ourselves to molecular orbitals composed out of the atomic $1s$ orbitals ϕ_a and ϕ_b there are just two:

$$\psi = \phi_a + \phi_b$$

$$\chi = \phi_a - \phi_b.$$

The conventional m.o. method asserts that the ground state wave function is $\psi(1)\psi(2)$, corresponding to both electrons in the bonding orbital ψ . But there is another conceivable function $\chi(1)\chi(2)$, which has precisely the same over-all symmetry as the earlier one. If it were not for the interelectronic term $1/r_{12}$ these two wave functions would remain quite distinct and separate. But when the r_{12} term is explicitly included we say that the two configurations "mix" or interact, and we speak of configuration interaction. This represented by taking for the complete wave function a mixture

$$\psi(1)\psi(2) + \lambda\chi(1)\chi(2),$$

where λ is a coefficient of interaction, which can be calculated, and which varies from zero when the internuclear distance is small up to unity when the two atoms are completely separated. At the equilibrium separation its magnitude is such that the excited configuration $\chi(1)\chi(2)$ has a weight about one-sixth that of the lowest configuration $\psi(1)\psi(2)$. Now what is significant about this is that it is one way of taking into account the physical characteristic of the r_{12} -repulsions. For it has the effect of separating the electrons in a manner rather similar to, though less extreme than, the familiar Heitler-London expression $\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)$. We may say that configuration interaction is one device for correlating the positions of the two

electrons in a bond. It is, of course, most important that we should know which configurations are likely to be important in this connection. The matter has been dealt with by Lennard-Jones & Pople (41), who showed how the r_{12} repulsion in the Hamiltonian was responsible for introducing a significant degree of interaction between σ^2 and π^2 configurations. We shall have to return to this matter later when discussing large molecules.

Ab initio CALCULATIONS OF THE ENERGY

Attempts continue to be made to calculate molecular energies without any approximations. This means that the complete Hamiltonian must be used, and all integrals must be evaluated. With diatomic molecules this is still technically possible, though when there are more than two nuclei, the integrations are prohibitively long. The most complete calculation recently made is due to Bates (60) who considered the $1s\sigma-2p\sigma$ transition in H_2^+ . The matter is not obscured by any other electrons, and the wave equation is separable in spheroidal coordinates. Values of the energy gap and the transition moment were calculated for a wide range of internuclear distances, and the correct values so obtained were compared with the approximate linear combination of atomic orbitals (LCAO) treatment. Agreement is better than might have been expected.

Another accurate calculation was concerned with a system of four collinear H atoms. Taylor (61) used the m.o. method with inclusion of a wide range of configuration interaction. In the ground state it appeared as if this interaction was less important than in the case of H_2 . But by far the most impressive work of this kind is due to Mulligan (62) who studied CO_2 . All the 22 electrons were allotted to molecular orbitals, and an attempt was made to evaluate or estimate all the integrals involved. The appearance of the analysis is frightening, but the results, both for the ground and certain low-lying excited states, give grounds for hoping that, when better techniques are available for handling the large numbers of terms and of evaluating the necessary integrals, it may become possible to make reasonably good calculations of this kind for systems containing not more than three or four atoms. The evaluation of the integrals is the worst part of the calculations. But, thanks to the work of Rudenberg (63), Kopineck (64, 65), Mulliken (14, 66), Mueller & Eyring (67), Kotani *et al.* (68, 69), Buehler & Hirschfelder (70), Carlson & Rushbrooke (71), Barnett & Coulson (72), there is every hope that before long adequate tables will be available for most simple problems.

Before leaving this section we must refer to some recent ideas of Moffitt (73, 74). Moffitt starts out by realising that as the internuclear distance in a molecule is increased, the m.o. wave function goes over into a combination of neutral and ionic states for the separate atoms. [E.g., in H_2 the conventional m.o. $\psi(1)\psi(2)$ of page 12 goes over into 50 per cent of $H-H$ and 25 per cent each of H^+H^- and H^-H^+ .] Now it has been shown by Moffitt (24) that the energy of a negative ion is always calculated most unfavourably by the usual types of calculation. He suggests, therefore, that in so far as the

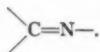
analysis will permit it, the true energies of the isolated atomic states should be used instead of the calculated energies. In the first paper (73) he is able to show that this can be done for the particular case of O_2 , and much improved excitation energies, such as for ${}^3\Sigma_u^- \rightarrow {}^3\Sigma_u^+$ are obtained. It is a corollary of this work that there is now much less configuration interaction than would otherwise have appeared to be necessary; so apparently configuration interaction in the older formulations not only separates the electrons of a bond, but also compensates for our relatively inaccurate theoretical atomic energies. In his second paper (74) the idea is extended. It is scarcely practicable to attempt more than a summary of the argument. But essentially Moffitt argues that, since the total molecular binding energy is often only a tiny fraction of the separate atomic energies, it would be most sensible to regard it as a kind of perturbation. Now in perturbation theory we expand the true wave function in terms of a series of wave functions corresponding to a Hamiltonian in which the perturbation term is not included. For the molecular case, these basic functions are the complete set of neutral and ionised atoms. The energies of these may be supposed known from experiment, even if our best wave functions do not adequately account for this energy. Presumably, since atomic states with a large excess of negative charge are extremely unstable, we shall be able to make an effective restriction on the totality of possible basic functions. When these are selected, the perturbation (caused by those terms in the potential energy which connect one atom with another) is introduced, and its magnitude is calculated using the approximate basic wave functions, but the true basic energies. Since the binding energy now appears as the perturbation energy, we avoid the difficulty so often met in other approaches to this problem, in which we obtain the binding energy as the relatively small difference of two very large terms. Here, on account of the fact that it is merely the perturbation energy, we may expect to get a reasonable value even without exceptionally good atomic wave functions. At the time of writing, insufficient numerical results are available to permit a final judgment on this most interesting proposal. But it is certainly attractive at first sight.

LARGE MOLECULES

Many of the ideas outlined earlier may be carried over to large molecules; by "large molecules" is usually meant conjugated and aromatic molecules whose planar character enables a distinction to be made between the σ -electrons, whose orbitals are symmetrical with respect to this plane, and the π -electrons, whose orbitals are antisymmetrical. It is usual to suppose that the σ -electrons are localised in approximately normal C—C or C—N (etc.) bonds, and that the π -electrons are mobile. It is this mobility which, by facilitating their movement from one atom to another, (a) makes possible the characteristic transmission of electrical influences all over the molecule, (b) provides a resonance dipole moment in addition to any σ -bond moments that may be present, (c) shifts the ultraviolet absorption into the near ultraviolet or visible region, and (d) causes the bonds to have lengths which are inter-

mediate between those of pure single or pure double bonds. Ever since it was recognised [Pullman (75)] that in these large molecules the Pauling resonance method is almost impracticable on account of the overwhelming importance of the heavily-excited component bond structures, the tendency has been to fall back on the m.o. method. This has recently been reviewed in these reports by Longuet-Higgins & Wheland (76), and will not be further described here. It may however be mentioned that a treatise has recently been published by A. and B. Pullman (77) which embodies practically all the immense number of calculations reported from the Paris groups working under Pullman and Daudel. It must suffice here to say that although the results of such calculations are generally correct in sequence and in general character, they are most unlikely to be accurate on an absolute scale to more than 50 per cent. The difficulties [see Coulson & Longuet-Higgins (78)] chiefly lie in our ignorance of the basic parameters which specify the difference between the electronegativity of carbon and any other hetero-atom, and the corresponding difference between the resonance integrals for the bonds. It is probable that, on account of the necessary approximations in the theory itself, no universally valid set of parameter values will be found. But Orgel, *et al.* (79) have recently suggested plausible sets that give correct dipole moments for several heterocyclic systems, and Löwdin (80) has shown how such values may be used with considerable facility in predicting other dipole moments. Other recent work in this field includes the discussion of additivity relationships for the energy resulting from OH substitution, by de Heer, Coulson & Evans (81, 82) and a careful and thorough analysis of all the small effects that might cause dipole moments in apparently homopolar molecules such as styrene or methyl-substituted aromatics, by Laforgue (83).

The question of bond lengths has been more carefully investigated. The need to do this arises from the greatly improved experimental technique which makes possible the estimation of these lengths in favourable cases, to within 0.01 Å. The present writer (84) has summarised the present position. Bond lengths are inferred from calculated bond orders and may be estimated to within 0.02 Å in most cases of pure hydrocarbons. A series of possible refinements are introduced which, as Coulson, Daudel & Robertson (85) showed for the particular case of naphthalene, will reduce the error a little further. In heterocyclic systems, as Cox & Jeffrey (86) point out, the chief trouble lies in our ignorance of the lengths of pure single and double bonds, especially



A peculiar feature of the hydrocarbon molecules is that the larger the molecule, the better apparently are the predictions [see Buzeman (87)].

When we attempt to determine the wave function for the π electrons by nonempirical methods, we find that configuration interaction appears to be exceedingly important. Several simple conjugated molecules like benzene and butadiene have been discussed by Craig, Coulson & Jacobs (88, 89, 90). The lowest configuration may only have a weight of 66 per cent, the other inter-

acting configurations accounting for the remaining 34 per cent. As Jacobs showed with naphthalene (91) this configuration interaction is responsible for a drastic reduction in the oscillator strength in certain of the electronic transitions. In this way, an old difficulty has been resolved. The interpretations of the excited levels is also greatly affected. References to other work of this kind, but chiefly without configuration interaction, are given by Mulliken & Parr (92). These latter authors show, as was first pointed out by Lennard-Jones (93), that the total resonance energy of molecules such as benzene must not be thought of in terms only of π electron energy, but allowance must be made for the considerable compression and extension of the σ -bonds in passing from a normal Kekulé structure to the final equilibrium bond lengths. For benzene, Mulliken & Rieke (94) showed that this compressional energy may be as large as 36 kcal./mole. This is almost as big as the net resonance energy 41 kcal./mole.

While discussing large molecules reference must be made to the beautiful work of Roothaan (95). Roothaan shows that the general self-consistent scheme approach of Lennard-Jones (53) can be set out in LCAO terms. Instead of looking for a set of self-consistent functions, we have now to look for a set of self-consistent coefficients. These can be found from a series of equations, fairly easy to write down, whose solution will in general have to be obtained by numerical means. The molecular symmetry, where it exists, enables the powerful methods of group theory to be applied, often with a considerable saving in time and corresponding gain in elegance. We look forward anxiously to seeing some detailed applications of this theory.

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RADIOACTIVITY AND NUCLEAR THEORY¹

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INTRODUCTION

One glance at the *Physical Review* shows that an enormous amount of work has been done during the last year in the field of radioactivity and nuclear structure. It is somewhat difficult to give the proper weighting in a review of this kind.

During the last year or two, our knowledge of nuclear structure has increased greatly. The quantum numbers of the ground states of many nuclei, that is, spins and parity, have been known for a long time. Recently, however, a great deal of information has been obtained about the quantum numbers of excited states. A regular nuclear spectroscopy has developed, quite analogous to the type of atomic spectroscopy of 1920. Knowledge of the quantum numbers of excited nuclear states is very important for the development of a theory of nuclei. The "spectroscopic" methods used are different for the long-lived, isomeric, states and for the short-lived ones. These methods are discussed extensively in the sections on isomerism and on angular correlation.

A consistent nuclear theory cannot be obtained as long as the forces between the nucleons are not known. It is generally believed that these forces, at least to a large part, are due to interactions with the field of π -mesons. The great advance in our knowledge of the properties of the π -meson is therefore the first step towards an understanding of nuclear forces. For this reason some experiments with mesons are discussed in detail.

ATOMIC MASSES

Three methods are available for the determination of atomic masses: nuclear reactions, mass spectrometry, and microwave spectroscopy of pure rotational spectra. Li *et al.* (1) have computed the masses of stable and unstable atoms over the range between the neutron and F^{20} , using only the data of nuclear reactions.

During the last year mass determinations by methods of mass spectrometry have been pursued most intensively by Nier and collaborators (1 to 5), Duckworth and collaborators (6 to 9), and by Ewald (10). Some work has also been done in Japan (11). Nier (1 to 5) has investigated systematically all stable atoms between S^{32} and Sc^{45} , as well as a number of lighter ones. Ewald's measurements (10) are mostly below mass 40. Duckworth (6 to 9) has concentrated on heavier nuclei, in particular on those in the neighborhood of the closed neutron shell of 82 neutrons.

¹ The survey of the literature pertaining to this review was concluded in January, 1952.

The method of mass determination by microwave methods is capable of giving the ratios of the masses of different isotopes of the same element only. Low & Townes (12) investigated atomic masses in the neighborhood of $A=40$. Recent work (13, 14) has extended the data in this region, and has included heavier nuclei. The three methods of measurement of atomic masses are in fairly satisfactory agreement with each other (12, 15, 16).

The net result of the great progress in this field is that one has, by now, a fairly complete knowledge of atomic masses, which means that the binding energies of the nuclei are known. The mass curve is not smooth, as the liquid drop model of the nucleus assumes, but shows the expected variations at the magic numbers (9).

NEUTRON BINDING ENERGIES

The energy with which the last neutron is bound to the nucleus can occasionally be determined from mass differences. Independent measurements, however, have been made in many cases. Values of the threshold energies in (γ, n) processes are direct measures of these quantities. Harvey (17) has tabulated neutron-binding energies of approximately 80 elements. About half of these were obtained by direct measurement of the (γ, n) threshold, the rest were obtained from (p, d) and other reactions. Harvey plots the difference of the measured values and those computed from the semi-empirical, Bohr-Wheeler mass formula. The deviations are very striking. Before the magic numbers, or closed neutron shells, 50, 82, and 126, the experimental binding energies, compared to the theoretical ones, rise, and beyond the magic numbers they drop sharply by about 2 Mev. This number for the discontinuity of binding energies is in good agreement with that obtained by Suess (51) from β -decay systematics.

In the meantime, many new (γ, n) threshold values have been accurately determined (18, 19, 20), mostly with the University of Pennsylvania beta-tron.

Investigation of the inverse reaction, namely the γ -rays emitted in neutron capture, has been continued mainly by a group at the Argonne National Laboratory (21 to 24) and at Chalk River (25 to 28). If direct transitions to the ground state occur, these are determined by the energy of the most energetic γ -ray. Thus one may obtain a measure of the binding energy of the added neutron. However, direct ground state transitions do not occur in all cases (28). The spectra observed are also a measure of the level density of the nuclei, and appear to be in good agreement with the liquid drop model. Great differences occur, however, near the magic numbers, where very few γ -rays are observed (25). Lead 207, for instance, in capturing a neutron to form the closed shell nucleus Pb^{208} , with 126 neutrons, emits only one γ -ray with an energy of 7.380 Mev, the binding energy of the 126th neutron. Bi^{209} , with 126 neutrons, also emits a single γ -ray of 4.170 Mev (26). Muelhouse (23, 24) reports that in several cases the γ -rays occurring are internally converted.

FISSION

In earlier investigations of the mass yield of fission fragments a smooth yield curve was obtained. This double-humped curve, with maxima at masses about 140 and 94 is very well known. Recently, however, mass spectrometric investigation (29, 30) has shown that the yield has considerable fine structure. Thode (29) and co-workers, in the investigation of the isotopic abundance of fission xenon, found a high yield at mass 133 and 134. Radiochemical studies on fission yields of Te and I also indicated a high yield for this mass (31). Glendenin, Steinberg, Inghram & Hess (32) investigated the isotopic abundance of fission zirconium and molybdenum and found a high yield at mass 98 to 100. On the assumption that 2.5 neutrons are boiled off in each fission act in U^{235} , this peak on the low mass hump is seen to correspond to the complementary fission product at mass 134, which is the point of exceptionally high yield on the hump of the large masses. Previously, attempts had been made to explain the exceptional yield of mass 134 by processes occurring after fission (33), connected with the low binding energy, and easy loss of a neutron outside the closed shell of 82. No such explanation can be found for the exceptional yield of mass 100. It seems, therefore, as if there is a preference for this particular division in the fission act.

It was reported last year that in the region of the medium heavy elements, reactions occur which are most properly described by the term fission. During this year, Batzel & Seaborg (34) showed that fission indeed occurs in a wide range of elements. The elements Cu, Br, Ag, Sn, and Ba were irradiated with protons in the Berkeley cyclotron. The fission of Sn yielded, for instance, Na^{24} , Ga^{66} , and Ga^{72} . The process known as "spallation," that is, a "boiling off" of small fragments, i.e., α -particles, neutrons, and protons, might yield such products. However, the threshold energy for fission would be considerably lower than for the corresponding spallation. It can thus be concluded that the process occurring is almost certainly one of fission. For instance, a calculated threshold for the production of Na^{24} from Sn^{118} is 50 Mev. The atom Na^{24} was definitely identified after bombardment with 100 Mev protons. Greenberg & Miller (35) bombarded copper with 370 Mev protons from the Columbia cyclotron and measured cross sections for the production of Be^7 , C^{11} , F^{18} , Na^{24} , Cl^{38} , and K^{42} .

 β -DECAY

Of the numerous investigations in the field of β -decay, only a few can be mentioned here.

Katcoff, Schaeffer & Hastings (36) have measured the lifetime of β -active iodine 129 and found it to be 1.72×10^7 years. This time is just long enough so that all the I^{129} that may have been on the earth at the time of its formation will have decayed to stable Xe^{129} . Acting on a suggestion by Suess (37), they used the lifetime of I^{129} to estimate the length of the time interval between the formation of the elements and the formation of the earth as 2.7×10^8 years. The age of the elements is then 3.6×10^9 years. The assump-

tions underlying the calculation are that originally as much I^{129} was formed as I^{127} ; that almost all Xe^{129} was produced by the decay of I^{129} ; that the radiogenic Xe^{129} leaked from the rocks into the atmosphere at the same rate as radiogenic A^{40} leaks from the rocks containing radioactive K^{40} . Xe^{129} has, for an odd nucleus, an unusually high isotopic abundance. Suess & Brown (38), however, point out that this may be due rather to the fact that the neighboring even isotopes of xenon have an abnormally low abundance. As a result, the value of 2.8×10^8 years for the time between element and earth formation can be regarded only as an approximate lower limit.

Pringle and co-workers (39) have extended their measurement of the decay process of the naturally occurring odd proton odd neutron isotope La^{138} . The nucleus converts by K -capture and emission of γ -rays to Ba^{138} . A decay scheme is proposed. The lifetime of La^{138} is given as 2.0×10^{11} years.

In 1949, Aston (40) showed that a weak, continuous γ -ray spectrum accompanies the phenomenon of β -decay. A satisfactory theory of the phenomenon was given in 1936 (41, 42) and extended by Chang & Falkoff (43) in 1949. The effect is due to the sudden change of the electric moment when part of the charge of the nucleus is released as a positron or electron, and is called internal *bremsstrahlung*. During this year, Madansky & Rosetti (44) studied continuous γ -radiation in P^{32} , and found that it agreed in intensity and spectral distribution with the calculations. Novey (45) studied the angular correlation of the β - and γ -rays, and Bruner (46) measured the internal conversion of the γ -rays. The most interesting application occurs, however, in the phenomenon of K -capture. Here, since the invisible neutrino carries off the excess energy, it is not possible to measure the energy change directly. The internal *bremsstrahlung* occurs in this case also (47). Its spectrum extends up to the maximum available energy, namely the energy change of the nucleus plus the rest-energy of the K electron. The shape of the spectrum has been calculated by Jauch (48). In a linearized plot of intensity versus energy, analogous to the Kurie plot in β -decay, it is possible to determine the end point of the spectrum, and hence the total energy change. Such an experiment has been performed by Bell and co-workers (49) on Fe^{65} . They find that the total intensity of the γ -rays is 3×10^{-5} per disintegration. The end point of the γ -ray spectrum determines the energy change in the transition as 206 ± 20 kev. This energy change has also been determined from the reaction $\text{Mn}^{55}(p,n)\text{Fe}^{55}$ as 217 ± 10 kev (50), which is in very good agreement. Thus it appears that the internal *bremsstrahlung* in K -capture is an effective method of energy determination.

The systematics of the energies involved in β -decay was investigated by Suess (51) and Jensen & Suess (52). For nuclei of odd A the total energy change (β -energy plus γ -rays) involved in a decay was plotted against the neutron number N of the initial nucleus for β -decay; against $N+1$, and with opposite sign, for β^+ -decay. Curves were obtained by connecting the plotted points for nuclei with the same neutron excess $N-Z$. These curves show very interesting regularities. They permit a fair estimate of the energy changes in nuclei where observation is still lacking. Very striking is the break in the

otherwise smooth curves at the magic numbers. The connection with shell theory is discussed (52). Suess (51) has extended the investigation to nuclei of even A , where a much more irregular behavior is found.

The systematics of transition probabilities of β -decay, on the basis of nuclear shell theory, has been published by Nordheim and co-workers (53). Nordheim (54) deduces from these data a rule for estimating the spin of nuclei with an odd number of protons and neutrons.

DOUBLE β -DECAY

Among the naturally occurring, apparently stable, nuclei of even atomic weight A , there exist numerous pairs and triplets of isobars (nuclei of the same A) which have even proton number and differ in charge by two units. Actually for given even A , one of the two or three nuclei of even Z must have the lowest energy. The other even isobars are actually metastable. That these even isobars are stable against direct β -decay has long been understood. The nucleus of intermediate charge has an odd number of protons and of neutrons, and the tendency of equal nucleons to pair up is responsible for the fact that its energy is higher than that of either of its neighbors. The metastable even isobar is then not able to decay directly by the emission of a single β -ray.

There exists, however, a method by which such metastable isobars are able to decay without violation of the energy principle. They may emit two β -rays simultaneously and thus go directly into the stable isobar, the charge of which is different by two units. Theoretical calculations of the lifetimes of such double β -transitions are ambiguous. If the β -interaction is of such a nature that two neutrinos are emitted with the two electrons (Dirac theory), the lifetimes are enormously long (55). For energy changes of the expected order, namely about 2 Mev, they are greater than 10^{24} years; for smaller energy changes they are even greater. If, instead, a neutrino is first emitted and then reabsorbed (Majorana theory), the lifetimes are shorter (56). Fermi (57) has made a number of calculations of lifetimes on this basis. For the transition from Sn^{124} to Te^{124} Fermi estimated an energy change of 2.2 Mev, and computed a half life of 2×10^{16} years. Similarly, the double β -transition from Te^{130} to Xe^{130} should have an energy of 1.6 Mev and a half life of 5×10^{16} years, that from U^{238} to Pu^{238} at 1 Mev a half life of about 10^{18} years. In 1949, Fireman (58) attempted to measure the double β -decay of Sn^{124} to Te^{124} by coincidence methods. He found a difference between normal tin and tin enriched in Sn^{124} , and from this obtained a lifetime of 9×10^{18} years.

During this year, this same transition was studied again; the result is in complete discrepancy with Fireman's. The lifetime is certainly longer.

The recent work was that of Kalkstein & Libby (59, 60), who also used the method of coincidence counting. Comparison was made between foils of normal tin, and of tin consisting of 95 per cent Sn^{124} . No difference in the coincidence rate was found. Assuming that the maximum activity is less than twice the standard deviation of counts, the half life of Sn^{124} for double β -emission is longer than 1.7×10^{17} years.

Lawson (61) examined tin enriched in Sn^{124} in a cloud chamber. No double β -decays were observed. The experimental condition and number of pictures taken were such that Lawson concludes that the half life is longer than 10^{16} years.

Seaborg and co-workers (62) investigated the occurrence of double β -decay of U^{238} to Pu^{238} . In this case, the energy difference can be rather reliably estimated as 1.1 Mev. From a very pure six-year-old sample of UO_3 plutonium was separated chemically. No α counts corresponding to Pu^{238} were found in the precipitate. This negative result leads to a half life for simultaneous emission of two β -particles from U^{238} greater than 6×10^{18} years.

Inghram & Reynolds (63) examined the isotopic constitution of xenon extracted from preCambrian tellurium ore. Te^{130} as well as Te^{128} are expected to undergo double β -decay to the respective xenon isotopes. Their results indicate a minimum half life of 1.3×10^{19} years for Te^{128} , and 8×10^{19} years for Te^{130} .

Altogether, it appears that the existence of double β -decay has not been demonstrated. The minimum half lives in the three cases investigated are longer by factors 10 or 100 than those computed on the basis of the Majorana theory. Unfortunately, these lower bounds are not yet high enough to allow one to make a definite decision between the two types of theories of β -decay. The calculations are really to be regarded as estimates only. One cannot be certain that selection rules may not make a particular transition slower than calculated.

INFLUENCE OF CHEMICAL STATE ON RADIOACTIVE LIFETIMES

There are two types of radioactive decays in which the orbital electrons of the atom enter directly. One is the process of K -capture, or capture by the nucleus of an orbital electron. The other is the phenomenon of internal conversion of the γ -ray of an isomeric transition. Here the energy of the nucleus is transmitted to an orbital electron, and this electron is ejected. In both these processes, a dependence of the lifetime on the chemical state of the substance may be expected. For both processes, such a dependence has been found.

The probability of K -capture depends on the density of electrons near the nucleus, and will presumably be effected by the chemical state in the lightest atoms only. Be^7 , which decays to Li^7 by K -capture, is therefore the best possible choice. Segré and co-workers (64, 65, 66) investigated the lifetime of the decay of Be^7 in different chemical compounds. In their experimental procedure, two samples containing Be^7 in different chemical compounds, but of as nearly as possible equal activity, were placed in two identical ionization chambers, and the difference of their activities was determined. It was found that the decay constant of beryllium oxide is smaller than that of metallic beryllium by 0.030 ± 0.018 per cent (65). Comparison of beryllium oxide and beryllium fluoride showed that the decay of beryllium in the oxide is faster by 0.1375 ± 0.0053 per cent (66).

Bainbridge, Goldhaber & Wilson (67) investigated the influence of the

chemical state on the lifetime of the isomeric state of technetium 99. The isomer has a lifetime of 6 hr. The energy is unusually low, namely only 2 kev. The γ -ray is almost entirely converted. It is followed by a prompt γ -ray of 140 kev, which can be conveniently measured.

The technique used by Goldhaber and co-workers is very similar to that used by Segré (68a). The difference in activity is measured as a function of time, for two samples, containing Tc^{99m} in different chemical compounds. The lifetime of technetium 99, when electrolytically deposited on copper, is longer by a factor 1.003 than that of Tc^{99} contained in dry KTcO_4 , and 1.0003 times larger than that for technetium sulfide.

The energy of this particular isomeric transition (2 kev) is lower than the binding energy of an electron in the atomic K or L shell. Conversion of the γ -ray can consequently happen from the M and higher electron shells only. Since the γ -ray is almost entirely converted, the main part of the transition probability depends on the probability of the ejection of an orbital electron out of one of these outer shells. Slater (68) calculates that the electron orbits involved are, in order of decreasing importance, the $3p$, $3d$, $4p$ and $4d$ orbits. The $4d$ electrons take part in chemical binding, and their wave functions will be thoroughly altered in different compounds. However, since the behavior of the wave function near the nucleus is responsible for the degree of internal conversion, Slater's calculations indicate that the observed effect is of the correct order of magnitude. In detail, the problem is complicated, and it is not even easy to predict the sign of the effect.

ISOMERISM

In recent years, many accurate measurements (69 to 78) have been made of the energies and lifetimes of long-lived nuclear isomeric states. It has long been recognized that such isomeric states occur when among the lowest energy levels of a nucleus there is one of a spin very different from the others. A nucleus in the level of different spin, that is, in the isomeric state, can then return to the ground state only by a radiative transition which is highly forbidden. As an example, the lowest states of Xe^{129} have spins $1/2$, $3/2$, and $11/2$ in that order. The state of spin $11/2$ decays into that of $3/2$ with a half-life of eight days. For a spin change of four, dipole, quadrupole, and octopole transitions are forbidden, and the transition can take place only by 16th pole radiation. The lifetime for this transition is increased over that for a dipole by the sixth power of ratio of the wavelength to the nuclear size. In addition, the radiative transitions are classified as being electric or magnetic. Magnetic transitions of a given pole are slower than the corresponding electric ones. The lowest radiative multipole order which is allowed for a given transition depends also on the change of parity (Table I).

Usually, the γ -ray of the isomeric transition is highly converted; a fraction of the excited nuclei do not undergo a radiative transition, but return to the ground state by transferring their energy to one of their orbital electrons. Thus, an electron is ejected from the K , L , or even higher atomic shell. The measurements of the energy of the isomeric transition are usually made

TABLE I

LOWEST ALLOWED RADIATIVE MULTIPOLE TRANSITION FOR SPIN CHANGE $\Delta I = L$

Parity Change	L even	L odd
Yes	2^L magnetic	2^L electric
No	2^L electric	2^L magnetic

by observing the line spectrum of these conversion electrons.

Up to this year there seemed to exist considerable inconsistencies in the interpretation of the data. The work of Goldhaber & Sunyar (79) has brought considerable order into this field. A clear picture of the experimental facts and reliable information about the spins and parity of the nuclear states involved has been obtained.

There are three methods for determining the degree to which the transition is forbidden, that is, the multipole character of the radiation.

(a) The conversion coefficient, that is, the ratio of the number of electrons to the number of γ -rays depends on the multipole type and on the energy. Accurate theoretical curves (80) have been calculated for different multipole types of the conversion coefficient versus energy. Comparison of the measured conversion coefficient with the theoretical one determines the type of radiation involved. However, these measurements are difficult and are performed accurately only in few cases.

(b) The electrons ejected from the K shell and the L shell may be observed and their intensity compared. This K to L ratio can be determined rather easily and accurately. The ratio depends on the multipole character, and the energy and the nuclear charge Z as Z^2/E . Only nonrelativistic and rather unreliable theoretical curves of the K to L ratio are available; the experimental data very often lie between two of these theoretical curves. Goldhaber & Sunyar (79) have substituted empirical curves in place of the theoretical ones. In plotting all available K to L ratios against Z^2/E , they find that all experimental points define rather accurately a number of smooth curves. All cases which have the same multipole order as determined by method (a) lie on the same curve, and thus define the order for the particular curve. Thus it is now possible to determine the spin change and parity change from measured K to L ratios.

(c) There exists a theoretical relation between the lifetime and energy of radiative transitions (81, 82, 83). The lifetime of a 2^n pole transition is proportional to the inverse $2n+1$ power of the energy, and to the square of a nuclear matrix element which should be roughly proportional to the n or $(n-1)$ power of the nuclear radius. Thus for a given nuclear radius, the theoretical curve of the logarithms of the lifetimes plotted against the logarithm of the energy form straight lines, with slopes equal to one plus twice the multipole order. For a given energy the lifetimes of transition types 2^n and $2^{(n+1)}$ differ by factors of at least 10^6 . Magnetic 2^n pole transitions are slower than electric 2^n pole by about 10^3 . Thus one is able to determine the

multipole character of the radiation from the lifetime even though one expects that the variation of the nuclear matrix element would give rise to scatter of the order of factors of 10 or 20. The agreement between this method and the others is very good. On the whole, one finds that electric transitions, compared to magnetic ones, live longer than expected. The numerous transitions identified as magnetic 16th pole show a curious characteristic. The logarithms of their lifetimes, when corrected for nuclear size, internal conversion, and obvious statistical factors, lie amazingly accurately on a straight line in the theoretical plot. The nuclear matrix elements involved vary by factors less than 1.5. This is an astounding and unexplained result.

Thus it is now possible to assign with confidence spin and parity values to isomeric states. These values are of great significance for a theoretical understanding of nuclear structure.

The experimental data are in very good agreement with the independent particle model of the nucleus (84 to 87). This model can make definite predictions for nuclei of odd atomic weight only. It predicts that isomerism should occur only in certain "islands," namely in those nuclei in which the odd neutron or proton is somewhat lower than one of the magic numbers 50, 82, or 126. Since the stability of the magic numbers is presumably due to the fact that spin-orbit coupling splits levels with large angular momenta in such a way as to lower appreciably those of high j , the levels of high spin occur just before the magic numbers, in competition with the lowest spins of the previous shell. Thus in particular, the islands of isomerism in odd nuclei should occur when the odd N or Z is between 39 and 49, between 63 and 81, and between about 100 and 125. The experimental data are in complete agreement. No long-lived isomerism is known in odd nuclei outside these islands.

In detail, the competition between 39 and 49 is between a $g_{9/2}$ and $h_{1/2}$ orbit. The spin change of four and change in parity predicts magnetic 16th-pole transition. Many such transitions are observed. However, electric octapole transitions are observed also, but only in cases in which more than one nucleon (or less than one hole) occupies the $9/2$ orbit. Since several particles in a $9/2$ shell are able to couple their spins in various ways (88) (for instance, to a resultant of $7/2$), this fact is not unexpected.

In the second island, between 63 and 81, numerous transitions of the magnetic 16th-pole type are observed, but only in odd neutron nuclei. The ground states of the stable nuclei of this type, as determined from spins and magnetic moments, are here either $d_{3/2}$ or $s_{1/2}$. In addition, the shell model predicts that orbits of the type $h_{11/2}$ fill in this region, and consequently have low energy. The isomeric transitions are all experimentally interpreted as a decay from the $h_{11/2}$ state to $d_{3/2}$. In many instances, and in all cases where the ground state is known to have a spin of $1/2$, the isomeric transition is followed by a second γ -ray, leading from $d_{3/2}$ to $s_{1/2}$, as has to be the case.

The level order obtained from the study of isomerism is in complete agreement with the shell model. The theoretically predicted states, and no

others, are observed. By a literal interpretation of the nuclear shell model it is possible to calculate the lifetimes of some isomeric transitions exactly. The nuclear matrix elements can be evaluated by the use of square well eigenfunctions. Here, however, the quantitative agreement is poor. The theoretical lifetimes are too short by a factor of about 20. The extreme constancy of the matrix elements for transitions of magnetic 16th-pole type cannot be explained.

Hill (89) has made a study of the dependence of the energy of isomeric transitions on the neutron and proton number and found some interesting regularities.

ANGULAR CORRELATION EXPERIMENTS

There is no sharp distinction between an "isomeric" state and other excited nuclear states. In the last section, experimentation on states with measurable lifetimes was discussed. There exist, however, other methods of determining the quantum numbers, that is, the spins and parity, of short-lived excited states. The angular intensity distribution of a γ -ray is spherically symmetrical, owing to the fact that all orientations of the spin of the excited state are equally probable. However, in a strong magnetic field, and at very low temperatures, the Boltzmann factor weights some spin orientations more than others, so that the emitted radiation is no longer isotropic. The theory of this effect was given by Spiers (90). Experiments have been performed in a highly specialized cryogenic laboratory by Daniels, Grace & Robinson (91), and the existence of the anisotropy of the radiation was definitely established.

If two or more successive radiations are emitted by a nucleus, there exist measurable phenomena which depend critically on the quantum numbers of the states involved. This was first pointed out by Dunworth (92). If only those transitions are observed in which the first γ -ray is emitted in a definite direction, the different spin orientations of the intermediate level are no longer equally probable, and the intensity of the second γ -ray is no longer isotropic. The intensity distribution of the angular correlation is a measure of the spin changes in the transition. The theory of γ - γ correlations was worked out by Hamilton (93). In his paper, angular correlation functions were given for specific sets of the angular momenta of the three states, and for low multipole order of the emitted quanta. At that time, however, neither sources of sufficient strength nor detectors of adequate sensitivity were available and the first attempts to discover correlation effects (94, 95, 96) could not give conclusive results. The first successful observations were reported in 1947 by Brady & Deutsch (97), who could avail themselves of scintillation counters instead of GM tubes. The work of these authors was followed by quite a number of successful investigations (98), and today γ - γ coincidence counting is a standard technique.

Experiments in which merely the angular correlation between the directions of propagation is observed can only give information on the angular momenta which the quanta carry away (i.e., their so-called multipole or-

ders), but not on the parity of the electromagnetic waves (i.e., the electric or magnetic character of the "multipoles") emitted. This is due to the fact that electromagnetic waves carrying the same angular momentum of either parity have the same distribution pattern—they differ essentially only in an interchange of E and H . Their difference is thus a purely transversal one and can experimentally be detected only through polarization effects. Thus in order to distinguish uniquely, say, electric and magnetic dipole radiations, the correlation between the directions of emission and the planes of polarization must be measured. Such a measurement contains obviously the maximum amount of information about two successive γ -emissions.

The theory of polarization-propagation correlations has been worked out by Falkoff (99) and by Hamilton (100) in 1948. To detect these effects a convenient "Nicol" for γ -rays had to be devised. This was achieved by Metzger & Deutsch (101), who made use of the angular dependence of Compton recoil electrons on the polarization of the incoming quantum.

One of the complications of γ - γ correlations comes from the fact that in many cases either or both of the transitions $j_1 \rightarrow j_2$ and $j_2 \rightarrow j_3$ can take place—owing to the vector addition principle—by quanta of different angular momentum though of the same parity. For instance, the transition $1^+ \rightarrow 1^+$ can take place with quanta of one or two units of angular momentum of $+$ parity, i.e., by magnetic dipole or electric quadrupole. These radiations, even if greatly different in intensity, perturb each other's distribution patterns strongly through interference. Directional correlation formulae, taking these effects into account, were first independently given by Fierz (102) and Ling & Falkoff (103), the latter giving explicit results. Zinnes (104) has extended these considerations to direction-polarization correlations.

As discussed in the section on Isomerism, quanta emitted in nuclear processes are always more or less "converted," i.e., accompanied by electrons (e^-) ejected from the atomic shell surrounding the nucleus. It is intuitively understandable that these electrons should also be emitted, in each transition between sublevels, with certain angular distributions and that hence γ - e^- and e^- - e^- angular correlations should be observable. These correlations have been calculated independently by Ling (105), Berestetsky (106), and Fierz (102), and most extensively considered by Gardner (107). The effect was observed by Ward & Walker (108) and by Frauenfelder, Walter & Züti (109).

In principle, nuclear radiations of other than electromagnetic nature (e.g., β , α) are also susceptible of producing directional correlation effects. It is, however, an advantage of electromagnetic radiation that it cannot be emitted at all with zero angular momentum, i.e., as a spherically symmetrical s -wave, because it is obvious that such a total isotropy of either radiation in a cascade forfeits any possibility of a correlation. Particle waves can be s -waves, and hence many cascades involving particle radiations will not exhibit correlation phenomena at all. This and many other very general features of correlation problems have been worked out in a paper by Yang (110), following ideas of Teller.

β - γ correlations have been theoretically investigated by Falkoff & Uhlen-

beck (111). They are an excellent additional tool for investigating the degree of forbiddenness of β -decays and the nature of the fundamental β -interaction. In an allowed β -transition, for instance, the particles are emitted as s-waves and for the reasons indicated above no β - γ correlation can occur, whatever the nature of the γ -ray. On the other hand, in forbidden spectra the correlation will depend, at least for certain types of interaction, on the velocity of the electrons. The phenomenon of β - γ correlation was successfully investigated by Grace, Allen & Halban (112), Garwin (113), Frankel (114), Walter, Huber & Züti (115), Novey (45), Stevenson & Deutsch (116), and others. Stevenson (117) and Darby & Opechowsky (118) have displayed the dependence of β - γ correlation on the energy of the electron.

α - γ correlations are, owing to the fact that the α -particle has no spin, particularly easy to calculate. Owing to the long half lives of most α -emitters, these correlations are perhaps of less general applicability than the types discussed before. Experimentally, such correlations have first been measured by Kulchitsky and collaborators (119), B. T. Feld (120) and, in a case where the α -particle is emitted in a nuclear reaction, by W. R. Arnold (121) and Barnes, French & Devons (122).

There are no known instances where a nucleus would decay by a fast successive emission of two α -particles, and hence α - α correlations—though theoretically the simplest ones—have received little attention. V. L. Telegdi (123) has measured α - α correlations in the decay of C^{12} highly excited by γ -rays.

The increasing success of the experimentalists in detecting angular correlations and the value of their results to nuclear spectroscopy has stimulated theoreticians to work out general formulae and tables embracing all probable nuclear spins and radiations of various angular momenta rather than to calculate the correlations resulting in particular situations. Successive steps in this direction are the papers of Spiers (124), Falkoff & Uhlenbeck (111), Racah (125), and Lloyd (126).

While in isomerism a measurable lifetime is the essential feature, in angular correlation experiments the intermediate state should be as short-lived as possible in order to avoid any reorientation of the nucleus before the second radiation is emitted. Such a reorientation can, e.g., take place through coupling with the electronic shell in the manner well known from hyperfine structure. The theoretical basis for such effects was given by Goertzel (127). Fortunately, in most cases the hyperfine coupling is too weak to produce an appreciable precession of the nucleus. An atomic shell in an 1S state has no hyperfine coupling, and many atoms are in such a configuration in their ground state. When the nucleus emits a particle, however, the electronic shell is perturbed (even ionized) and might not recover before the second emission takes place. If the perturbed shell is coupled strongly enough with the nucleus, the resulting angular correlation might depend on the speed with which the shell recovers, and thus in last analysis, on the material in which the atom is embedded. This "chemical effect" has been discovered by Frauenfelder (128, 129).

MESONS

For several years π -mesons, or pions, have been produced artificially. The π^+ - and π^- -mesons have the same mass, namely 276 electron masses. The mass of the neutral π^0 -meson is smaller by about 11 electron masses. It is usually assumed, on the basis of their similar production cross section and from the evidence of the charge independence of nuclear forces, that the fundamental transformation properties, namely the spins and parities, of these three pions are alike.

In 1951 an important milestone was reached: it was established that the spin of the π^+ -meson is zero, and that the parity of the π^- -meson is odd. From the assumption of the basic equality of the mesons, it is then concluded that all three types of pions have these properties, which are usually summarized in the statement that the pions are pseudoscalar.

It has been shown previously for all three charges of π -mesons individually that they obey Bose statistics, and, in units of $h/2\pi$, have integral spin, not half-integer. For π^- -mesons this follows, for instance, from the experiments of Panofsky, Aamodt & Hadley (130) in which protons are captured by π^- -mesons. A sharp γ -ray peak is observed corresponding to the reaction (p stands for a proton, n for a neutron)

$$\pi^- + p \rightarrow n + h\nu. \quad 1.$$

Since the sum of the reaction products on the right-hand side obey Fermi statistics, the sum of the products on the left-hand side must do so too. Since the proton is a Fermi particle, the pion must obey Bose statistics. The total angular momentum of the products on the right side of equation 1 is certainly half-integer, because of the intrinsic spin of the neutron. The principle of conservation of angular momentum requires that the angular momentum of the left-hand side is also half-integer, a conditions which can be accomplished only by an integer spin of the pion.

The same conclusions may be drawn for the π^0 -meson from the fact that in the above-mentioned experiment another reaction competes with equation 1 and occurs in about 50 per cent of the cases, namely

$$\pi^- + p = n + \pi^0. \quad 2.$$

For the π^+ -meson, Bose statistics and integral spin follow in the same way from the photoproduction of mesons

$$p + h\nu = n + \pi^+. \quad 3.$$

The π^0 -meson decays into two photons. From this property it follows (131, 132) that its spin, in units of $h/2\pi$, cannot be unity.

The conclusion that the spin of the π^+ -meson is zero was reached by the comparison of two sets of experiments and some theoretical reasoning which is independent of any meson theory but depends exclusively on the principle of detailed balancing (133, 134). In Berkeley, hydrogen was bombarded with 340-Mev protons (135, 136, 137). π^+ -mesons were observed. Their spectrum, measured in the forward direction, extends from energies of about 18 Mev to 75 Mev. The intensity is rather constant up to 65 Mev, and then shows a

sharp peak at 70 Mev. The continuous spectrum is attributed to the reaction



The sharp peak arises from the monochromatic pions which occur in the formation of the deuteron, d ,



The cross section of this reaction was measured. The inverse of reaction given in equation 5



the absorption of π^+ mesons by deuterons, has been observed both by the Columbia and the Rochester group (138, 139) at the meson energy of 22.7 Mev; this corresponds to the same energy in the center of mass system as bombardment by 340 Mev for the reaction of equation 5. Consequently, the two cross sections, that of 5 and that of the inverse reaction 6 at 22.7-Mev meson energy, ought to be very simply related. Each cross section is proportional to the phase volume of the reaction products and to a matrix element. According to the principle of detailed balancing the two matrix elements must be the same, and the ratio of the cross sections for the two reactions depend on the phase volume only. The phase volume of reaction 5 depends on the meson spin s . The relation is obtained

$$\frac{\sigma(\pi^+ + d \rightarrow p + p)}{\sigma(p + p \rightarrow \pi^+ + d)} = \frac{2}{3} \frac{K^2}{k^2} \frac{1}{2s + 1}$$

where K and k are the momenta of the proton and meson respectively in the center of mass system.

The experimental value of the cross section for the absorption of π^+ -mesons by deuterons obtained by Roberts and co-workers (139) is 4.5 ± 0.8 millibarns. From the Berkeley results on reaction 5 one would predict the absorption cross section to be 3.4 ± 0.9 mb. assuming a spin of zero, and 1.1 ± 0.3 mb for a spin of unity. The results for spin one are quite outside the experimental error. The spin of zero for the meson has thus been established.

The odd parity of the negative pion is deduced from another experiment of the Berkeley group (130). Negative π -mesons, absorbed by deuterium, give rise, in about 30 per cent of the cases, to the reaction



In this reaction no γ -ray is observed. The other 70 per cent lead to the emission of two neutrons and a γ -ray. Because of their negative charge, π^- -mesons are captured by positive nuclei and traverse Bohr orbits around them (smaller than those of the electrons by a factor of the ratio of the mass of the electron to that of the meson). The meson will eventually find itself in the lowest orbit, a $1s$ orbit, or K orbit. In this state, the spin of the left-hand side of equation 7 is just that of the deuteron, namely one in unit of $\hbar/2\pi$. Conservation of angular momentum requires that the decay products also come off with angular momentum one. The only such state which the Pauli

principle allows for two neutrons of spin one-half is 3P_1 , a state of odd parity. Parity must be conserved. The deuteron is even, and so is a K orbit. Consequently the decay can take place if and only if the parity of the pion is odd.

Thus it is established that the pion is pseudoscalar if the decay actually takes place from an s orbit. This is the only doubtful point in the argument, since a decay from a p orbit is allowed for particles of even parity. Theoretical calculations by Serber and co-workers (140) seem to show that the ordinary radiative transitions from higher Bohr orbits to the $1s$ state are much faster than the rate of nuclear reactions from these excited states. It seems very probable that the decay does take place from the meson K -shell, and that the above argument for the odd parity of the π -meson is correct.

These results about the nature of the π -meson are of great importance for nuclear theory. Since π -mesons interact strongly with nuclei, it is hoped that π -mesons are responsible for the major part of nuclear forces.

A tremendous amount of work has been done with artificially produced π -mesons, too much to be reported here. For the first time, some of the products obtained in the reaction of π^- -mesons with nuclei were chemically analyzed. Turkevich & Niday (141) found that carbon 11 is produced by the action of π^- -mesons on O^{16} and N^{14} . Work with photographic plates loaded with uranyl acetate shows that π^- -mesons produce fission in uranium. Al-Salam (142) estimates that fission occurs nearly every time a π^- -meson is absorbed by U^{238} . Brueckner (143) has shown that it is possible to interpret the scattering of pions by hydrogen as an indication of excited states of nucleons.

Cosmic ray work has indicated the existence of an appreciable number of species of mesons heavier than the π -meson. All mesons known up to now, and some of their properties, are listed below.

The μ -meson exists as μ^+ or μ^- . Its mass is 210 electron masses, its lifetime 2.1×10^{-6} seconds. μ^+ decays into a positron and two neutrinos, μ^- into an electron and two neutrinos.

π^+ normally decays into μ^+ and a neutrino, with a half life of 2.6×10^{-8} seconds. The μ^- -meson usually ends its life by being captured by a nucleus and producing a star. π^0 decays into two photons, with a much shorter half life of 10^{-14} second.

The τ -meson is a charged particle which is seen to decay into three particles of electronic charge, probably π -mesons. On the assumption that the decay products are actually π -mesons, the mass of the τ -meson is 966 electron masses. The lifetime is very crudely estimated as 10^{-9} seconds.

Evidence for K -mesons is still somewhat scanty. Their properties are that they come to rest in the photographic plate and emit a charged meson, which, at least in one case, has been identified as a μ -meson. In addition, one or two neutral particles must be released. The mass of K -mesons is about 1200 electron masses. It is an open question whether there exists just one type, or whether there are two types of K -mesons, designated as K_1 and K_2 . The half life seems to be of the same order of magnitude as that of the τ -meson.

These data have been taken from references (144, 145, 146), where other literature references are given.

The existence of a neutral particle, designated as V^0 , with a mass larger than that of the proton, has been very well established. The V^0 -particle decays into two charged particles, which, in many cases, have been identified as a positive proton and a negative π -meson. It is of interest to note that negative protons have not been observed. In some cases V^0 -particles are seen to disintegrate into a positive and a negative pion. If no neutral particles are involved in the decay, and there is some evidence that there are none, there must be two types of V^0 -mesons, V_1^0 and V_2^0 . The mass of V_1^0 is 2210 electron masses, that of V_2^0 about 700. The half life of the V^0 -meson is 3×10^{-10} seconds. There is some indication of the existence of charged V -particles. The observations were mainly undertaken by groups at Manchester, California Institute of Technology, Berkeley, and Indiana University (147, 148, 149).

It begins to look as if the universe contained a very large number of metastable, "fundamental" particles of which we are able to observe only those which, by some accident, have a low probability of decay.

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ISOTOPES¹

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INTRODUCTION

There is a considerable range of interests in researches connected with the fundamental properties of isotopes as well as with the uses of isotopes. Any review of the literature on isotopes must therefore be somewhat restrictive and will usually reflect the interests of the reviewer. This review covers the general field of the chemistry of isotopes, i.e., studies of the physical state and the chemical properties of matter which are affected by the nuclear mass. Knowledge of the abundances of isotopes and their masses is important to such studies and a review of the progress of these subjects is therefore included.

MASS MEASUREMENTS

There has been considerable progress in the precise determination of nuclear masses. Li, Whaling, Fowler & Lauritsen (1) have compiled a table of masses for nuclides up to mass 20 based entirely on nuclear reaction data. The estimated uncertainties range from three to thirty micro mass units. There is very good agreement between this table of masses and the one of Ewald (2), which is derived from mass spectrographic determination of doublets. Ewald's compilation utilizes his determinations of some of the important doublets of the light elements, which were carried out with a resolution of 25,000 to 40,000. Ewald also measured some new doublets involving O^{17} , O^{18} , Ne^{20} , Ne^{22} , P^{31} , S^{34} , and Cl^{38} . Nier and his students have described a double focusing mass spectrometer which utilizes electrical recording (3), as well as measurements made with this instrument. Their later measurements, in which they have studied the effects of focusing and the kinetic energy of the ion fragments (4), give a value for the proton mass in substantial agreement with Li (1) and Ewald (2). There is still disagreement on the mass of C^{12} and the value of the doublet $C^{13}H^1-O^{16}$ between Nier (4), Ogata & Matsuda (5), and Mattauch and Bieri (see ref. 4) on the one hand and Ewald (2), Bönisch (6), and Li (1) on the other. Nier has called attention to the need for additional measurements on this important doublet. The earlier masses reported from Nier's laboratory (7, 8) are in error in part because of the cycles chosen by them. Wapstra (9) has shown that Roberts' cycle (8) is

¹ This review covers the calendar year of 1951 and was prepared at the Brookhaven National Laboratory under the auspices of the United States Atomic Energy Commission. The coverage of foreign journals is incomplete as many issues of these were not available in this country at the time this review was prepared.

in agreement with other data if the value for the doublet $C^{12}H_4-O^{16}$ is taken from nuclear reaction data.

Collins, Nier & Johnson (4) have measured a considerable number of new doublets in the region of mass 40 and find good agreement with other data such as nuclear reaction data, the Bohr-Wheeler formula, and the ratio of Cl^{35}/Cl^{37} obtained from microwave spectroscopy. There is a serious discrepancy for the Q value of the reaction $Ca^{42}(d, p)Ca^{44}$ as determined from nuclear reaction data and mass spectroscopic measurements.

Duckworth & Preston (10) have measured the packing fractions, by the doublet technique, of nuclides in the neighborhood of magic number nuclei. They find a minimum in the packing fraction at $^{28}Ni^{60}$, a break in the curve at $A=90$, which may be at $^{40}Zr^{90}$, a change in the slope of the curve at $^{50}Sn^{120}$, and a break at $^{82}Pb^{208}$. The additional stability of all of these nuclides are predicted by the nuclear level scheme of M. G. Mayer (11) but not by those of Nordheim (12) or Feenberg (13).

In the past few years considerable effort has been devoted to increase the precision of mass measurements of medium and high atomic weight nuclides. Instruments which measure the time of flight of ions in a magnetic field or the cyclotron frequency are capable of a precision which is independent of the mass of the ion, in contrast to conventional spectrometers, where the precision decreases with increasing mass. Hays, Richards & Goudsmit (14) have achieved a precision of one to two millimass units in the measurement of some nuclides ranging from S^{32} to Xe^{134} . They have also given a detailed analysis of the factors limiting the precision of a time of flight spectrometer. Smith (15) has described a mass spectrometer with which he has measured the mass of S^{32} to one millimass unit and expects to increase the precision by a factor of ten with a larger instrument.

ISOTOPIC ABUNDANCES

Graham *et al.* (16) have determined the absolute abundances of the germanium isotopes with an accuracy of 0.5 per cent and the relative abundances to 0.1 per cent. Six different ores were studied and all gave the same results except GeO_2 from zinc ores of the Joplin, Missouri district, which had the light isotopes favored. The intensities of the $GeCl^+$ and GeF_3^+ ions from $GeCl_4$ and GeF_4 respectively were measured. Their results are in good agreement with the previous measurements by Inghram (17) on Ge, and Hibbs (18) on GeF_4 and GeI_4 , except for the ratio of Ge^{76}/Ge^{73} which Graham *et al.* find greater than unity. All of the mass spectrographic data lead to an atomic weight between 72.63 and 72.65, whereas the International Atomic Weight is given as 72.60.

Rakestraw, Rudd & Dole (19) have continued the work on the variation of O^{18} in the atmosphere. They have measured the isotopic composition of O_2 dissolved in the Pacific Ocean as a function of depth. They find a maximum in the O^{18} concentration and a minimum in the amount of dissolved O_2 at a depth of about 800 m. They suggest that the enrichment in O^{18} and the depletion in dissolved O_2 results from metabolism by marine vegetation, plank-

ton, bacteria, and other sea life and that O^{16} is metabolized faster (3 per cent) than O^{18} .

Milatz, Kluyver & Hardebol (20) have reported the determination of C^{13} by measurements on the 4.3μ band of CO_2 in an instrument designed for the analysis of simple gaseous mixtures by infrared absorption. For samples containing one to ten per cent C^{13} an accuracy of 20 per cent in the C^{13} abundance has been obtained and an increase of a factor of ten in the accuracy is anticipated by the use of a double beam instrument. If the latter is achieved, the method could serve as an alternate for mass spectrometric analysis in many cases.

ISOTOPE SEPARATION

Several important works have appeared this year on the theory of isotope separation processes. The volume on the theory of isotope separation by Cohen (21) in the National Nuclear Energy Series has been published. This book presents a logical development of the theory of multistage separation processes with a small enrichment factor in each stage. The basis of the theory is the conservation of matter. The theory concerns itself with the productivity, enrichment, equilibrium time, hold up, and the control problem of both ideal and real cascades. There is a chapter on the fundamental equations of the centrifuge and a discussion of evaporative, concurrent, and countercurrent centrifuges. There is a discussion of the behavior of liquid-gas countercurrent chemical exchange columns in terms of the film transfer coefficients. Finally, there is a derivation of the equations of the Rayleigh distillation in one of the appendices. The book should prove valuable to all concerned with the combination of separative elements in a multistage operation.

Majumdar (22) has found an exact solution of the equations of the thermal diffusion column without the restriction of low concentration of one of the components. The theory gives good agreement with the experimental measurements of Clusius & Dickel (23) on the rate of approach to equilibrium of a column separating air into its constituents. Dickel (24) has derived the equations for the thermodynamic efficiency of isotope separation processes by the use of the methods of the thermodynamics of irreversible processes and applied them to the analysis of the thermal diffusion column. Here again good agreement is found with experiment.

Several papers have been published on isotope separation processes and equipment. Keim (25) has reviewed the past five years of production of enriched stable isotopes with the calutron, and his report lists the quantities and purities of enriched isotopes available from the Atomic Energy Commission from this operation. There is a report of a small plant that has been set up at the Scientific Research Institute in Tokyo (26) to produce ten per cent N^{15} by the exchange between NH_3 and NH_4^+ . The engineering study by North & White (27) on the plate efficiency and the separation factor for the concentration of S^{34} by the sulfur dioxide-bisulfite ion exchange in packed towers has been mentioned in Stewart's review (28).

Klemm (29, 30) has continued his studies of isotope separation by electrical migration in molten salts. In one set of experiments the light isotopes of zinc were enriched by the electrolysis of molten zinc chloride in a cell which had solid lead chloride in the catholyte compartment. From these experiments the diffusion constant of Zn^{++} has been calculated. In another experiment Li^6 was enriched from 7.3 per cent to 16.1 per cent by electrical migration in molten lithium chloride.

At the National Bureau of Standards 99.8 per cent pure HD has been prepared (31) by the reaction of LiAlH_4 with D_2O and subsequent fractional distillation.

ISOTOPE EFFECTS ON PHASE EQUILIBRIA

In the past few years there has appeared a considerable addition to the literature on the thermal properties and vapor pressures of hydrogen, both as affected by isotopic substitution and equilibration with respect to the *ortho* and *para* states. Most of this work has been carried out at Los Alamos Scientific Laboratory, National Bureau of Standards, and the Ohio State University Cryogenic Laboratory. Workers in these laboratories have published seven papers this year on the subject. Grilly (32) has measured the vapor pressures of solid $n\text{-H}_2$, $n\text{-D}_2$ and $n\text{-T}_2^2$ and of the liquid forms of these substances up to 3 atm. He has also measured the densities of liquid T_2 between 20.6° and 29°K . (33) with an estimated accuracy of 0.2 per cent. At the Bureau of Standards (34) the vapor pressures of $e\text{-H}_2$, HD and $e\text{-D}_2$ have been measured from the triple points to the critical temperatures. Also the vapor pressures of a sample of $n\text{-D}_2$ was measured between 21° and 34°K . Dew points of mixtures of $n\text{-H}_2$, HD, and $n\text{-D}_2$ were measured between 17° and 20°K . Positive deviations, of the order of 3 ± 1.5 per cent, were found from the laws of ideal solution. These workers (35) have also measured P - V isotherms in the neighborhood of the critical temperatures of $e\text{-H}_2$, HD, and $e\text{-D}_2$. There is a pronounced difference in the shapes of the domes in the P - V diagrams for the hydrogen molecules and substances like CO_2 . The Ohio State group have measured the thermal properties and vapor pressures of $e\text{-D}_2$ from 13.1° to 23.6°K . (36), the vapor pressures of $n\text{-D}_2$ between the boiling point and critical point (37), and have arrived at an empirical correlation of the freezing points, boiling points, and critical points of the isotopic $n\text{-H}_2$ molecules in terms of their molecular weights (38). They have also intercompared the vapor pressures in terms of these fixed points by the use of two constant vapor pressure equations and a Dühring chart. The procedure is completely empirical and, therefore, no theoretical significance can be attached to it.

Intercomparison of the vapor pressure data from these laboratories indicates some serious areas of disagreement. If the discrepancies are interpreted in terms of differences in temperatures, then one finds that data of Grilly (32) and of Hoge & Arnold (34) on $n\text{-D}_2$ agree to within ten millidegrees. The data of Kerr, Rifkin, Johnston & Clarke (36) on $e\text{-D}_2$ show a temperature

² The prefix n refers to material in equilibrium with respect to *ortho* and *para* species at 300°K ., while the prefix e refers to material equilibrated at 20.4°K .

discrepancy which decreases from 0.11°K. at 19°K. to 0.05° at 23.5°K. from those of Hoge & Arnold (34). The data of Friedman, White & Johnston (37) on $n\text{-D}_2$ show a temperature discrepancy of 0.11°K. from $23^{\circ}\text{--}27^{\circ}\text{K.}$ from those of Grilly (32). These discrepancies indicate that the Los Alamos temperature scale is in excellent agreement with that of the Bureau of Standards, while that of the Ohio State University Cryogenic Laboratory is lower by about 0.10°K. It is clear that additional work will be necessary to bring these temperature scales into closer agreement. It is difficult to estimate which scale is most closely correct.

The discrepancies between Grilly's vapor pressure data on $n\text{-T}_2$ from those calculated by Hammel (39) indicate the inadequacy of the semiempirical quantum corrections of de Boer (40) to the law of corresponding states.

Becker & Stehl (41) have intercompared the gas viscosities of $e\text{-H}_2$ at 283°K. and $e\text{-H}_2$ at 77°K. to test the theory of Halpern & Gwathmey (42). According to this theory, there should be a difference of 0.8 per cent between the viscosities of these gases because of a quantum correction to the collision cross section. Previous experiments by Harteck & Schmidt (43) found no effect as large as 0.1 per cent. The differential measurements of Becker & Stehl indicate a difference of $7.4 \pm 0.7 \times 10^{-2}$ per cent. The experiments are being continued to obtain more information about this difference.

New measurements confirm the suggestion that liquid He^3 is the stable form at 0°K. Osborne, Abraham & Weinstock (44) have determined the melting curve of He^3 between 1.02° and 1.51°K. by the blocked capillary technique. Extrapolation of the data to lower temperatures, where additional experimental work is being carried on, indicates no triple point down to 0°K.

Mazur & Prigogine (45) have applied the methods of the thermodynamics of irreversible processes to the hydrodynamics of solutions of He^3 in He^4 . Their method is a general one, and if one applies the restriction of inhibition to momentum transfer, then one obtains the hydrodynamic equations of Gorter (46) directly. The theory gives good agreement with the experimental observations on the effect of He^3 on the fountain effect in He^4 (47, 48).

A monograph by Kirshenbaum (49) reviews the literature on the physical properties and analysis of D_2O . The book contains one chapter on physical properties, one on equilibrium constants for exchange reactions involving H_2O , HDO , and D_2O , three chapters on the analysis of heavy water by various means, and finally one chapter on the natural abundance of the isotopes of hydrogen and oxygen. Included in the compilation is a considerable body of experimental data accumulated at Columbia University under the Manhattan Project and released to the public in this monograph for the first time. The book is extremely detailed and the chapters dealing with the mass spectrometric analysis of the isotopes of hydrogen in the form of H_2 give complete diagrams of all parts of the spectrometers used at Columbia, many of which are now obsolete. In many respects the monograph is outdated by developments in this field since the end of the war. No data published after 1945 have been included. Nevertheless, the volume should prove

to be a useful compilation. The extensive discussion of the analysis of water for deuterium should prove helpful to the uninitiated, even though it is in many respects obsolete.

Schrader & Wirtz (50) have redetermined the relative densities of D_2O and H_2O between 20° – $100^\circ C.$ to $1/20,000$. Their results are in substantial agreement with Kirshenbaum's compilation.

It has been known for some time that there is a hysteresis loop in the lambda transition in NH_4Cl (51) but none in the corresponding transition in ND_4Cl (52). Thomas & Staveley (53) have investigated the effect of particle size and deuterium substitution on the transition. Powders and crystals of NH_4Cl , NH_3DCl (prepared from NH_3 and DCl), ND_3HCl (prepared from ND_3 and HCl), and ND_4Cl were studied. The transition temperature was found to vary linearly with deuterium substitution and the hysteresis loop decreases with deuterium content. In the case of NH_4Cl an increase in the crystal size was found to increase the width of the hysteresis loop. Upon resublimation of the partially deuterated salts, the transition became more diffuse. This result may have come from an increase in the crystal size or a disproportionation of the partially deuterated salt to give a mixture of five salts. It is not certain whether the deuterium in the samples of the partially deuterated salts before resublimation were distributed in accord with the stoichiometric formulae or were in statistical equilibrium among the different NH_4^+ ions.

Some definitive experiments on the superconductivity of separated mercury and tin isotopes have been reported by Reynolds, Serin & Nesbitt (54) and by Maxwell (55) respectively. Both studies show that the critical temperature for superconductivity, T_c , varies inversely with the square root of the mass of the isotope. These results support the theories of Frohlich (56) and Bardeen (57), where superconductivity is attributed to an interaction of the conduction electrons with the lattice vibrations.

ISOTOPE EFFECTS IN CHEMICAL EQUILIBRIA

There is a limited number of molecules for which there are sufficient spectroscopic data to make a calculation of isotopic exchange equilibria with an accuracy of better than 1 per cent in the deviation from random distribution ($K/\sigma - 1$). In many cases, even when the molecular parameters of the individual isotopic molecules are known, the anharmonicity coefficients are not, and they can introduce errors of this magnitude. Recently a sufficiently accurate potential function for N_2O was established (58, 59) to provide the basis for the calculation of the partition function ratios of the isotopic N_2O molecules and some exchange equilibria involving N_2O (59). McCrea (60) has carried out some calculations on N_2O which serve to illustrate the importance of the anharmonic and interaction terms in the potential function.

Stranks & Harris (61) have published a preliminary report of their measurements on the exchange equilibrium



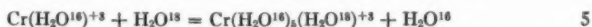
At 25°C. the equilibrium constant is 0.886 at pH 9 and 0.892 at pH 10.

In a study of the exchange of hydrogen between D_2 and CH_4 catalyzed by nickel, Kembell (62) allowed some samples to come to equilibrium and measured the equilibrium constants for the reactions



in the neighborhood of 740°K. As one would expect a priori for isotopic disproportionation equilibria at high temperatures, the equilibrium constants are close to those predicted by classical statistics (random distribution). Kembell has also calculated the equilibrium constants from spectroscopic data and made an approximate correction for the anharmonicity by assuming that this correction is similar to that in water. The deviation of the experimental equilibrium constants from the calculated ones varies from 2 to 10 per cent. Part of this disagreement is due to the scatter in the experimental data.

Hunt & Taube (63) have carried out a very interesting study of the exchange of water between hydrated cations and the solvent. In the course of this investigation they have made some observations on fractionation processes involving water. Samples of solvent water were removed by distillation at 25°C. for analyses. In the distillation of 20 per cent of the water from pure water, they find $N_o/N_D = 1.005$, where N_o and N_D are the mole fractions of H_2O^{18} in the original sample and distillate respectively. From the theory of the Rayleigh distillation and the relative vapor pressures of H_2O^{18} and H_2O^{16} this ratio should be 1.007. The discrepancy may be ascribed to analytical errors and possibly entrainment in the distillation. In a similar experiment, where the solvent is 4.5 *M* in $NaClO_4$ and 1.45 *M* in $HClO_4$, this ratio became 1.009. The change is significant and in accord with theoretical expectations. The heavy isotope concentrates in the species with the strongest binding (64). For solutions containing Al^{+3} , Ga^{+3} , and Th^{+4} at high concentrations, this ratio varies between 1.010 and 1.016. The addition of these ions to water should improve the separation of O^{18} by the fractional distillation of water. Most of the work of Hunt & Taube deals with the slow exchange of $Cr(H_2O^{16})^{+3}$ with H_2O^{18} in the solvent. At equilibrium they find



$K_5 = 6(1.03)$. The larger fractionation factor in this case as compared with those mentioned above is consistent with the stronger binding of the first hydration sphere to Cr^{+3} and the slow exchange of this water with the bulk solution. All of the other ions exchange their water rapidly.

Becker & Vogell (65) have determined the relative solubilities of $HC^{12}N^{14}$, $HC^{13}N^{14}$, and $HC^{12}N^{15}$ in glacial acetic acid, where there is no polymerization. The relative solubilities of $HC^{13}N^{14}$ and $HC^{12}N^{15}$ as compared with $HC^{12}N^{14}$ were determined from the operation of a countercurrent distillation column of an undetermined number of theoretical plates at an unspecified tempera-

ture. Since the height of a plate is the same for $\text{HC}^{13}\text{N}^{14}$ and $\text{HC}^{12}\text{N}^{15}$, an analysis of the top and bottom of the column gives the ratio of the fractionation factors for these two isotopic species relative to $\text{HC}^{12}\text{N}^{14}$. If we consider the quantity $\epsilon = \alpha - 1$, where α is the relative solubility of one of the heavy HCN molecules compared with $\text{HC}^{12}\text{N}^{14}$, then Becker & Vogell find for the ratio $\epsilon(\text{HC}^{13}\text{N}^{14})/\epsilon(\text{HC}^{12}\text{N}^{15}) = 1.74 \pm 0.3$. Becker & Vogell have also determined the absolute value of $\epsilon(\text{HC}^{13}\text{N}^{14})$ by means of a Rayleigh distillation and find a value of $1.9 \pm 0.6 \times 10^{-3}$. The fact that the ratio $\epsilon(\text{HC}^{13}\text{N}^{14})/\epsilon(\text{HC}^{12}\text{N}^{15})$ differs from unity is indicative of the fact that the change in the vibration frequencies between the gas and solution plays a dominant role in the magnitude of the fractionation factor. If only the intramolecular forces were important, then the ratio $\epsilon(\text{HC}^{13}\text{N}^{14})/\epsilon(\text{HC}^{12}\text{N}^{15})$ would be identically unity. By making the assumption that the difference in each of the vibrational frequencies between any isotopic pair in the liquid is proportional to its difference in the gas phase, Becker & Vogell calculate 1.81 for the ratio $\epsilon(\text{HC}^{13}\text{N}^{14})/\epsilon(\text{HC}^{12}\text{N}^{15})$. This assumption is in accord with the Kirkwood theory for the effect of solvation on vibrational frequencies (66).

Urey and his associates (67, 68) have continued their investigation of paleotemperatures of marine life by the CO_3^{2-} — H_2O temperature scale. This scale depends on the fact that there is a small, but measurable, temperature coefficient for the exchange equilibrium of O^{18} between CaCO_3 and H_2O . In one paper (68) they have set up a temperature scale by the analysis of CaCO_3 from marine animals which grew at known temperatures, which varied between 7.4° and 31°C . This temperature scale agrees with the one established previously (69) for inorganically precipitated CaCO_3 . Measurements of the ratio of $\text{C}^{13}\text{O}^{16}\text{O}^{18}/\text{C}^{12}\text{O}_2^{16}$ can be made with a precision of 0.02 per cent, which corresponds to an error of $\pm 1^\circ\text{C}$. The errors in temperature determination are limited by other phenomena at present. For instance, variations in the O^{18} content of ocean waters amounting to 17 per cent have been found, which would correspond to a temperature variation on the CO_3^{2-} — H_2O scale of 10°C . The O^{18} content of ocean waters varies linearly with salinity, a correspondence which seems plausible inasmuch as factors which tend to increase one also increase the other. An attempt is being made to develop the PO_4^{3-} — H_2O thermometer, which has a different temperature coefficient from the CO_3^{2-} — H_2O scale. If this is successful, then samples of CO_3^{2-} and PO_4^{3-} which were in equilibrium with the same water will suffice to determine the temperature and will eliminate the uncertainty in the composition of the water.

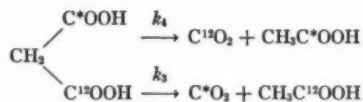
Since the temperature scale established from CaCO_3 of marine origin agrees with that determined by inorganically precipitated CaCO_3 , it is safe to assume that O^{18} exchange equilibrium is achieved in marine growth. It has been found that large crystals of calcite, such as belemnite specimens, preserve the temperature record over long periods of time. In one experiment samples of CaCO_3 were ground from a belemnite shell as a function of the radius from the center. Seasonal variations in the growth of the animal were found and four winters and three summers could be identified. Furthermore, it was established that the animal died in the spring.

The growth temperatures of some belemnites, brachiopods, and oysters from the Upper Cretaceous of England, Denmark, and southeastern United States were determined. The results are entirely of geological interest and will not be discussed here.

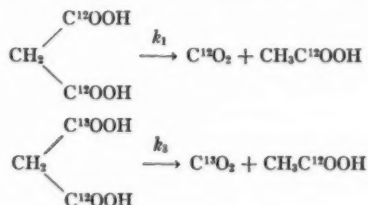
ISOTOPE EFFECTS IN CHEMICAL KINETICS

During the past few years the tempo of activity in the determination of isotope effects on reaction rates has been constantly increasing as a result of improvements in experimental techniques, the wider distribution of enriched isotopes (stable and radioactive), and renewed theoretical interest in the problem. The carbon isotope effect in decarboxylation reactions has received particular attention.

The four papers published last year on carbon isotope effects have done a great deal to clarify our understanding of these effects. Previously, Yankwich & Calvin (70) had measured the C^{14} isotope effect in the decarboxylation of malonic acid at 150°C . and of brom-malonic acid at 115°C . Their reactions were carried to completion and they measured the relative rates of the following two processes:



It was pointed out by Bigeleisen (71) that the ratio k_4/k_3 can be calculated rather precisely from the theory of the relative rates of reaction of isotopic molecules (72) without any assumptions regarding either the normal molecules or the transition state. These calculations led to a value of 1.020 for k_4/k_3 where C^{13} is the label, and 1.038 where C^{14} is the label. Subsequent experiments by Bigeleisen & Friedman (73) on the decarboxylation of malonic acid containing one atom per cent C^{13} (natural abundance) gave a value of 1.020 for the ratio of k_4/k_3 , in excellent agreement with theoretical predictions. These authors also measured the ratio of the rates of the reactions



They found $k_1/2k_2$ equal to 1.037 at 137°C . The theoretical calculation of this ratio, which requires a model, was in poor agreement with experiment. Subsequently Pitzer (74) proposed a model for the decarboxylation reaction which led to the values of 1.14 and 1.07 for C^{14} and C^{13} substitution respectively at 150°C . In Pitzer's model the ratio k_4/k_3 varies appreciably with temperature and is equal to $k_1/2k_2$.

Roe & Hellman (75) have repeated the experiments of Yankwich & Calvin on malonic acid with C^{14} at 153°C . They report a considerable scatter in their experimental data with a value of k_4/k_3 equal to $1.06 \pm .02$ from the average of their ten best runs.

Lindsay, Bourns & Thode (76) have repeated and extended the work of Bigeleisen & Friedman (73) on the C^{13} isotope effect in the decarboxylation of natural malonic acid. Their results are in quantitative agreement with those of the latter authors.³ In addition they find the ratio k_4/k_3 independent of temperature, a condition which is just what had been predicted by Bigeleisen (71) and contrary to Pitzer's model. They also found that C^{13} is randomly distributed in natural malonic acid, as was assumed to be the case by Bigeleisen & Friedman.

Bothner-By & Bigeleisen (77) have measured the relative rates of decarboxylation of carboxyl- C^{12} and $-C^{13}$ mesitoic acids at 61° and 92° and find the ratios $1.037 \pm .003$ and $1.032 \pm .001$ at these temperatures. They have also discussed the application of the theory of isotope effects in reaction kinetics to the decarboxylation reaction. Bigeleisen & Allen (78) have made a precise study of the relative rates of decarboxylation of $1-C^{12}$ and $1-C^{13}$ trichloracetate ions at 70°C . The $1-C^{12}$ ion was found to decompose $1.0338 \pm .0007$ times as fast as the $1-C^{13}$ ion. These authors have also discussed the errors which arise in the determination of the relative rates of reaction of isotopic molecules. Neither of these two studies supports Pitzer's model.

Ropp, Weinberger & Neville (79) have measured the C^{14} isotope effect in the dehydration of formic acid by concentrated sulfuric acid. The ratio of the C^{12} to C^{14} reaction rates varies between $1.125 \pm .005$ at 0° and $1.094 \pm .006$ at 25°C . The relative rates are of the correct order of magnitude for this reaction. The temperature coefficient is somewhat larger than one would expect from theoretical calculations and may in part be due to an underestimate of the precision of the measurements.

Weigl, Warrington & Calvin (80) report that $C^{14}\text{O}_2$ is assimilated 0.83 times as rapidly as $C^{12}\text{O}_2$ in photosynthesis with barley shoots. The system is too complex to warrant further interpretation at this time.

Harris (81) has considered the general kinetics of isotopic exchange reactions. Where there is no isotopic specificity, the McKay first order law is obtained. In the general case the kinetics are those of a reversible chemical reaction. For the case where the tracer is present at low concentration, the kinetics are those of a first order reaction and the half-life is dependent on the equilibrium constant for the exchange reaction and is not given simply by McKay's law.

Jones (82) has made a very careful study of the relative rates of photochlorination of H_2 and HT . It is well known that the slow step in this reaction is the reaction of hydrogen molecules with chlorine atoms. HT can react with

³ Lindsay, Bourns, and Thode report a value of $k_1/2k_3$ at 138° of 1.046. Subsequently Dr. J. G. Lindsay has communicated to this reviewer the results of a more extensive study of this ratio. The ratio was studied between 137° and 196°C ., found to be independent of temperature, and equal to 1.036 ± 0.003 .

chlorine atoms to give either HCl or TCl. In Jones' work the relative rates of the H_2 and the sum of the two HT reactions were measured. The ratio of the rate constants k_H/k_T was found to be

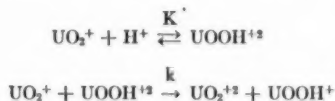
$$k_H/k_T = 1.35 \pm 0.03e^{865 \pm 7/RT}$$

Jones has compared this ratio with calculations based on the potential energy surface for this reaction constructed by Wheeler, Topley & Eyring (83). The theoretical calculations are in poor agreement with experiment. The sign of the temperature coefficient of the relative rates is incorrectly predicted and the calculated ratio of the frequency factors exceeds the experimental value considerably. Jones points out that the triangular complex suggested by Magee (84) may give better agreement with experiment.

Van Meersche (85) has reinvestigated and extended the measurements of Farkas & Farkas (85a) on thermal conversion of *para* hydrogen to *ortho* hydrogen and the exchange between H_2 and D_2 . These reactions proceed by the reaction of atoms from the thermal dissociation with the molecule. The new results are in substantial agreement with those of Farkas and Farkas but the larger temperature range leads to a better value of the activation energy. In addition, Van Meersche has used a better value for the heat of dissociation of H_2 and as a result finds that the activation energy for the reaction between atom and molecule should be lowered from 7.6 to 7.2 kcal. A calculation is then made for the relative rates of some of the isotopic reactions of hydrogen atoms with hydrogen molecules. The agreement with the calculations of Hirschfelder, Eyring & Topley (86), and of Farkas & Wigner (87) is improved. There is a significant discrepancy in the reaction between deuterium atoms and molecules. Some of this discrepancy may in part be due to the heat of dissociation of D_2 used by Van Meersche, which does not agree too well with that of Woolley, Scott & Brickwedde (88).

Gilman, Dunn & Hammond (89) have found that ϕ_3SiD hydrolyzes six times as rapidly as ϕ_3SiH at room temperature. They attribute this large reverse effect to the displacement of a hydride ion in the silane and the formation of something similar to a hydrogen molecule in the transition state. The ratio of the partition function of HD and H_2 is not large enough to explain so large an effect and it is probable that water, which has a large ratio for the partition functions of HDO and H_2O , is involved in the transition state.

Duke & Pinkerton (90) have measured the relative rates of disproportionation of U^{+6} in light and heavy water. The rate is 1.7 times as fast in D_2O as in H_2O . The mechanism of the disproportionation reaction is believed to be



Duke & Pinkerton interpret the isotope effect as the result of the increased base strength of UO_2^+ toward deuterons as compared with protons. The ex-

planation seems quite plausible and is of the correct order of magnitude for such a process.

Post & Hiskey (91) have measured the deuterium overvoltage in solutions of DCl in D_2O on a mercury cathode as a function of temperature and current density. These data when combined with similar ones on the protium overvoltage give an electrolytic separation factor of protium from deuterium of 3.1 at $20^\circ C$., which is in excellent agreement with the direct experimental determinations of Horiuti & Okamoto (92a) and of Walton & Wolfenden (92b). This agreement supports theories which postulate that one particle is involved in the discharge process and rules out a slow step which involves the combination of two or more entities at the electrode.

Mason, Biddick & Boyd (93) have measured the effect of ultrasonic radiation on the electrolytic separation coefficient of deuterium from protium at a polished platinum cathode. The radiation was found to increase the separation factor and decrease its temperature coefficient. This has been interpreted in terms of inhibition of the exchange reaction between H_2 and HDO, which is believed to take place to some extent at the electrode. This back exchange decreases the separation factor and is presumably retarded by the removal of gases from the electrode surface by the ultrasonic radiation.

Bell & Caldin (94) have measured the rates of decomposition of nitramide and nitramide, containing 40 to 60 atom per cent deuterium, in anisole catalyzed by dimethylamine between 0° and $45^\circ C$. The study was undertaken to look for evidence of reaction by quantum mechanical leakage through the potential barrier. Such leakage is anticipated for a reaction where the rate-determining step is proton transfer. Leakage should manifest itself in a large increase in the frequency factor. No such effect was found and the difference in rates can be explained by a difference in activation energies of 1800 calories/mol. The experiments were unfortunately complicated by the fact that the nitramide was far from completely deuterated.

Taylor & Dibeler (95) have studied catalyzed and exchange reactions of H_2 and D_2 with olefins on nickel. The rate of the shift of the double bond in butene-1 is four times as rapid in the presence of H_2 as in the presence of D_2 at $60^\circ C$. This ratio drops to 2.5 at $130^\circ C$. Isomerization of *cis*- and *trans*-butene-2 proceeds at identical rates in the presence of H_2 and D_2 . There is still insufficient information on these interesting but complex reactions to interpret these results.

ISOTOPE EFFECTS ON MASS SPECTRA

Stevenson (96) has determined and discussed the mass spectra of the propanes and butanes containing one carbon atom enriched in C^{13} . From the spectra of the monoisotopic ions and the assumptions of no C^{13} isotope effects on the parent ions or in the rupture of C—H bond, it is possible to work out a mass spectrometric analytical method for $-C^{13}_0$, $-C^{13}_1$, and $-C^{13}_2$ in propanes and butanes. Isotope effects in the rupture of C—C bonds on electron impact are found and discussed qualitatively in terms of two effects to be

discussed below in connection with the mass spectra of the deuteroparaffins. It is interesting to note, as Stevenson points out, that the C_1 fragments from $C_3H_8^+$ and the C_1 and C_2 fragments from $i-C_4H_{10}^+$ are independent of the labeling in the original skeleton. The mass spectra of the isomeric C^{13}_1 compounds are identical in these fragments.

Stevenson & Wagner (97) have intercompared the mass spectra of all the C_1 to C_4 monodeuteroparaffins with the corresponding protium compounds. All the deuteroparaffins show isotope effects on bond rupture by electron impact. These are discussed in terms of two effects: (a) the application of the Franck-Condon principle to the transition from the ground state to an excited one which leads to ionization; (b) the relative dissociation probabilities of ions of the type ABA'^+ into AB^+ and $A'B^+$, where A and A' are isotopes of the same element. These two effects serve to explain the fact that the dissociation probability at D in CH_3D is lower than H in CH_4 , after correction for a statistical factor of four, while the dissociation probability of H in CH_3D is higher than in CH_4 . It is not possible to account for the entire mass spectra of the deuteroparaffins by the assignment of two parameters, one for the decrease in the dissociation probability of deuterium and the other for the increase in the dissociation probability of protium in the deuteroparaffin.

Lossing, Tickner & Bryce (98) have measured the difference in the ionization potentials of some protio- and deuterio-paraffins. No difference is found between the pairs $C_2H_2-C_2D_2$ and $C_2H_4-C_2D_4$. The methanes show a linear increase in ionization potential on deuterium substitution, amounting to 0.18 volts between CD_4 and CH_4 . From zero point energy considerations alone, this would require the force constants in CH_4^+ to be but one-fourth those in CH_4 , an unreasonable requirement. The authors suggest that part of this difference might be explained in terms of the Franck-Condon principle. This difference in ionization potential limits the applicability of the method suggested by Stevenson & Wagner (99) for the analysis of mixtures of protio- and monodeutero-paraffins to successive pairs in the deuterio-methane series (100). The method of Stevenson & Wagner utilizes low energy electrons so that only the parent ions are produced. The difference in ionization potentials, if small, as between successive pairs in the deuterio-methane series, is negligible. When it amounts to 0.18 volts, errors are introduced. It appears that this limitation of the method of Stevenson & Wagner applies only to the methanes.

Dibeler & Bernstein (101) have intercompared the mass spectra of $CHCl_3$ and $CDCl_3$ obtained with 50 to 70 volt electrons. The C-H bond ruptures 3.0 times as frequently as the C-D bond. The ratio of HCl^+/DCI^+ from the two molecules is 1.6, while there is no effect of deuterium on the probability of rupture of C-Cl bonds.

Ploch & Walcher (102) have determined the yield of electrons by the impingement of positive ions (electron multiplier tubes) as a function of the mass of the positive ion. They have derived a correction formula to be applied to abundance determination of positive ions with electron multiplier tubes.

TABLE I
 ISOTOPE SHIFTS IN MOLECULAR SPECTRA

Authors	Reference	Subject
Hillger & Strandberg	(109)	Theory of centrifugal distortion in the rotation of asymmetric top molecules. Application to HDS.
Weiss & Strandberg	(110)	Microwave inversion rotation spectra of the deuterio-ammonias.
Nordman & Lipscomb	(111)	Theory of unit cell dimensions of LiH and LiD.
Lord & Nielsen	(112)	Infrared and Raman spectra of B_2H_6 , $B_2^{10}H_6$, and $B_2^{10}D_6$.
Herzberg, Jones & Leitch	(113)	Photographic infrared spectrum of $CD_3C\equiv CH$.
Lohman, Reding & Hornig	(114)	Vibrations and crystal structure of H_2S and D_2S .
Lord & Ocampo	(115)	Raman spectrum of allene- d_4 .
Hedberg & Badger	(116)	Infrared spectra and potential constants of $HOCl$ and $DOCl$.
Crawford, Fletcher & Ramsay	(117)	Infrared spectra, structure, and force constants for CH_2N_2 and CD_2N_2 .
Reding & Hornig	(118)	Vibrational spectra of solid NH_3 and ND_3 .
Lancaster, Inskeep & Crawford	(119)	Infrared spectrum and assignments for $CH_2=CD_2$.
Cunningham, Boyd, Myers & Gwinn	(120)	Structure and dipole moments of <div style="text-align: center;"> $\begin{array}{ccc} CH_3-CH_2 & & CH_2-CH_2 \\ & \diagdown \quad \diagup & \\ & O & \end{array} \quad \text{and} \quad \begin{array}{ccc} CH_2-CH_2 & & CH_2-CH_2 \\ & \diagdown \quad \diagup & \\ & S & \end{array}$ </div> from the microwave spectra of the isotopic molecules.
Talley & Nielsen	(121)	Vibration-rotation spectrum of C_2D_2 . Suggest possibility of measuring a vibration-rotation difference band in the microwave region.
Condon, McMurry & Thornton	(122)	Infrared and mass spectra of $CH_3-CD(OH)-CH_3$, $CH_3-CDCl-CH_3$, $CH_3CD_2CH_3$, and $CH_3-CD(CH_3)-CH_3$.
McMurry & Thornton	(123)	Infrared spectra and vibrational assignments of $CH_3CD_2CH_3$, $CD_3CH_2CD_3$, and $CD_3CD_2CD_3$.
Tiers	(124)	Analysis of <i>o</i> -, <i>m</i> -, and <i>p</i> -deuterotoluenes by infrared spectra.
Porter	(125)	Band spectrum of DNO_2 and identification of band spectrum of HNO_2 .
Decius & Wilson	(126)	Sum rules for the vibrational spectra of isotopic molecules.
Fletcher & Arendale	(127)	Infrared spectra and vibrational assignments of parallel bands in CD_2CO and $CHDCO$.
Plyler & Gailar	(128)	Near infrared spectrum and structural parameters of C_2D_2 .
Charette & Hemptinne	(129)	Infrared spectra and vibrational assignments of the deuterioethylenes.

ISOTOPE SHIFTS IN ATOMIC AND MOLECULAR SPECTRA

Fred, Tompkins, Brody & Hamermesh (103) have investigated the hyperfine structure of HeI experimentally and theoretically. The observed structure conforms to a nuclear spin of one-half and a negative nuclear magnetic moment. The splitting of the 3S terms are in good agreement with theory, while the splittings of the 3P and 3D terms indicate perturbations from neighboring fine structure levels. The isotope shifts from He⁴ show deviations from those calculated by the Hughes-Eckart formula and are principally due to interactions between states.

The nuclear magnetic moment of Os¹⁸⁹ has been found to be 0.6 ± 0.1 n.m.u. by means of hyperfine structure measurements (104). A preliminary report of the hyperfine structure of ErI (105) shows the presence of lines resulting from Er¹⁶⁶, Er¹⁶⁸, and Er¹⁷⁰. The absence of Er¹⁶⁷ lines may be due to the large number of components of this isotope with nuclear spin $7/2$. The shift between Er¹⁶⁶ and Er¹⁶⁸ is equal to that between Er¹⁶⁸ and Er¹⁷⁰. The isotope shifts of U²³⁴ and U²³⁶ in the 4244 line of the arc spectrum of uranium have been measured (106). For the series U²³³, U²³⁴, U²³⁵, U²³⁶, and U²³⁸ the shift is strictly proportional to Δm .

Brix & Engler (107) have shown by a study of the hyperfine structure of GdI and EuI that the large isotope shifts found in the rare earths are not to be attributed to any peculiar property of the f electrons. Rather it results from the change in the nuclear volume after completion of the 82 neutron shell. By a study of the isotope shift in the CeII spectrum, Murakawa & Ross (108) have shown that the neutron number is more important than Z in determining the isotope shift in the spectra of the heavy elements.

In the field of molecular spectra and molecular structure, isotope shifts are valuable in the establishment of assignments of observed lines to transitions between energy states, the removal of certain degeneracies, and in the establishment of the potential energy function of the molecule. A detailed review of the progress in the use of isotopes in this field is a topic in itself. We shall record here in tabular form a brief abstract of the literature published in 1951.

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RADIATION CHEMISTRY

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Study of the chemical changes produced by high energy radiations has proved increasingly popular during the last year, as indicated by the large number of articles appearing on the subject. Previous reviews in this publication (1, 2) have indicated the nature of the major problems in the field. The present review covers only papers appearing or work performed during the year 1951.

The character of the problems of radiation chemistry depends upon the nature of the material being irradiated, and this review is arranged accordingly. A general review of the present status of experiment and theory in the field was published by Burton (3). A brief historical summary of radiation chemistry and its relation to the problems of radiation effects on living organisms was published by Allsopp (4).

RADIATION CHEMISTRY OF GASES

Interpretation of the yields of chemical change observed on irradiation of different gases constitutes a very difficult problem because of the great variety of processes which may occur. The most important processes are believed to be: (a) ionization of the molecule; (b) unimolecular breaking up of the ion simultaneously with the ionization process or after a certain interval of time; (c) capture of electrons by molecules with or without molecular dissociation; (d) transfer of charge from an ion to a molecule in the gas; (e) chemical reactions of ions with uncharged molecules (sometimes describable as charge transfer with dissociation); (f) dissociative combination of positive and negative ions; (g) molecular splitting without ionization (dissociation by excitation); (h) reactions of long-lived (metastable) excited atoms and molecules; (i) subsequent reactions of free radicals produced by all the above processes.

The problem of reaction mechanism is to find the extent to which each process contributes to the reaction for any given system. Essex and his students have been studying this problem for many years; their approach has been to determine the effect of an electric field on the amount of chemical change occurring under α -particle irradiation. The field attracts ions to the electrodes and should remove the ion recombination process from the picture. The project is at present being continued under the direction of Benjamin Burtt. In order to obtain more insight into the role of negative ions a charged grid has been added to the apparatus which should filter out free electrons and thus give information on the role of electron capture in the reactions (5). The effect of the electric field on the chemical yield has been shown to depend upon pressure for certain reactions; this pressure effect is especially promi-

nent in some unpublished work by Rudolph & Essex (5) on the decomposition of azomethane and shows that the relative importance of the ion recombination and direct excitation processes depends upon pressure. Work is proceeding on hydrogen sulfide, hydrogen-chlorine mixtures and other systems. The mechanisms have not been completely elucidated in any case, but the work is continuing actively and seems to offer the best available prospect for study of reaction mechanisms in gas-phase radiation chemistry.

The theory of the various individual processes is of great interest to radiation chemists. The theory of charge transfer for molecular ions was discussed by Magee (6). The poor state of present theory even for monatomic ions was pointed up by the experiments of Hasted (7) who determined the cross section for charge exchange in monatomic gases as a function of energy of the ions. Quantitative agreement with theory appeared in some cases but not in others; the picture is probably complicated by the existence of ions in metastable states. The only system studied involving molecules with more than one atom was the charge exchange between O^+ ions and N_2 molecules; unexpectedly large cross sections were found, attributed qualitatively to the participation of vibrational and rotational levels in the process. This effect is precisely what radiation chemists are interested in, but a theory capable of quantitative prediction seems rather far off at present. The theory of electron capture by molecules was discussed by Magee & Burton (8).

Experimental study of the rate of ion recombination in gases has made a great advance by the use of microwaves, whereby the electron density in a gas may be determined as a function of time. The most thorough studies by this method have been made on the noble gases, helium, neon, and argon. Even these cases show chemical complications. Biondi & Holstein (9) and Redfield & Holt (10) show that the homogeneous recombination coefficient in the noble gases is much too high to be explained by radiative capture of electrons by monatomic ions, and a large concentration of diatomic ions such as A_2^+ must be present. Presence of these ions has also been demonstrated by experiments on ion mobility by Hornbeck (11) and mass spectroscopic work by Hornbeck & Molnar (12). The diatomic ions arise by reactions of metastable excited atoms: $He^* + He \rightarrow He_2^+ + e^-$. The cross section for ionization by H_2^* or Ne^* appears to be surprisingly high, of the order of 10^{-16} cm^2 , according to Biondi (13). In Hg vapor there is little or no electron-ion recombination; some attachment of electrons to Hg atoms seems to occur according to Dandurand & Holt (14). Hydrogen was studied by Varnerin (15); the processes are naturally more complicated in a diatomic gas and complete elucidation does not seem to have been attained. Electrons apparently disappear by dissociative attachment to H_2 molecules as well as by dissociative recombination with H_2^+ ions.

The chemical effects of radiation must in general depend upon the local concentrations of ions or radicals formed in the track of the ionizing particles and therefore upon the mean ionization density of the radiation used (defined as number of ions produced per unit length of particle track). Magee (16) has set up a theoretical formula for consideration of such effects which applies to

liquid as well as gas-phase study. The essential point is to distinguish the part of the reaction occurring in the particle track, where the concentration of active species is high, from the background reaction produced throughout the irradiated volume by active species which have escaped from the tracks by diffusion. Either the background reaction or the track reaction may predominate. Liquids, or gases at high pressure, appear to fall generally in the low background category with reaction occurring chiefly in columns; gases at ordinary pressure may be in either category depending upon the ionization density of the radiation. For an understanding of such problems, studies on ionization and ion recombination in insulating liquids are of great importance. Experimental difficulties in studies of ionization in liquids were discussed by Taylor (17).

The polymerizations of vinyl chloride and of isobutene in the vapor phase under α -ray bombardment were studied by Mund, Herman & Huyskens (18). The ion pair yield was found to be proportional to pressure at the beginning of the reaction but to become proportional to the square of the pressure later in the reaction. Interpretation of the kinetics is uncertain because a cloud of polymer forms in the gas which greatly complicates matters. Polymerization of the same materials in the liquid state under the same radiation gives yields per unit energy input about 45 per cent greater than in the gas, according to Mund & Herman (19). The number of polymerization chains started is presumably about the same in the two phases.

Mund, Huyskens & Lories (20) have continued the study of the reaction $H_2 + D_2 = 2HD$ under α radiation. They find the unexpected result that the reaction is inhibited to nearly the same extent by a great variety of added gases, including O_2 , CO , CO_2 , NO , C_2H_6 , C_2H_4 , CCl_4 and many others. The reaction is certainly a chain carried by hydrogen atoms. Inhibition by the added gases, being independent of the chemical nature of the gas, must be caused by formation of a van der Waals complex between the added gas and the hydrogen atoms, rather than by chemical reactions of the atoms.

AROMATIC COMPOUNDS

The behavior of aromatic compounds under radiation is so different from that of other organic compounds that they deserve consideration as a special class. Aromatic materials generally show strong fluorescence and relatively little chemical change under radiation as compared to aliphatic compounds. The energy is presumably taken up largely by excitation of the shielded system of π electrons in the aromatic nucleus. For some years, the strong fluorescence of these compounds under excitation by charged particles has been utilized in scintillation counters, with anthracene crystals being the favorite material. In these counters a "pulse" of light produced when a particle traverses the crystal is received by a photomultiplier tube and the "pulse height" is a measure of the fluorescence yield. During the year, interest in anthracene counters centered about the relation of the efficiency of light output to the ionization density of the radiation. Frey and co-workers (21) determined the response of anthracene counters to protons of various

energies. Similar work by Taylor and co-workers (22, 23) confirmed Frey's data on protons and also gave data on α -particles, deuterons, and slow electrons. The different radiations are characterized by values of dE/dx , the energy lost by the particle per unit length traversed in the material. Taylor found on plotting light output against dE/dx that all the radiations fell on the same curve with the exception of the slow electrons which appeared to give less light than heavy particles of the same dE/dx . Birks (24) has developed a theory of the effect; he assumes that part of the energy produces damaged molecules of anthracene which act as quenchers of the fluorescence in the path of the radiation. The theory implies that the lifetime of the excitation which yields fluorescence is long compared to the time required to produce the damaged molecules, and that the excitation can migrate freely through distances at least as great as the average distance between damaged molecules. The concentration of the damaged molecules in the neighborhood of the particle track is BdE/dX , where B is a constant and the light yield $d(\text{light})/dX$ will be given by $AdE/dx/(1+kBdE/dx)$, where k is the quenching constant for the damaged molecules and A is another constant. The explanation agrees with Birks' data on α -rays and fast electrons and also with the data of Frey and of Kruger on heavy particles, but not with Kruger's data on slow electrons, the validity of which Birks is inclined to question. Birks & Black (25) show that on continued α -irradiation the efficiency of anthracene scintillations decreases due to accumulation of damaged molecules in the crystal, and follows the expected law $I_0/I = 1 + AN$, where N is the total number of α -rays which have passed into the crystal, I_0 and I are the initial and later light yields and $A = 10^{-11}$. From the magnitude of A , the damaged molecules must be at least 1000 times more effective as quenchers of the fluorescence than anthracene molecules.

Hengst (26) studied the temperature dependence of anthracene fluorescence with cathode rays and ultraviolet rays. The theory of anthracene fluorescence was discussed by Ageno & Querzoli (27). Observations which they consider especially significant are that decay of the fluorescence is exponential and the mean life increases with increasing temperature. The only reasonable picture consistent with both these facts is that excitation energy migrates through the crystal, but barriers exist arising from crystal imperfections which (at low temperature) confine the excitons to small regions and thereby decrease their lifetime; a rise in temperature enables the migrating excitons to surmount the barriers, and thereby increase their lifetime.

Koski & Thomas (28) determined the fluorescence efficiency and spectra for crystals of a number of aromatic compounds containing double bonds conjugated with the ring. In the series diphenylethane, diphenylethylene, and diphenylacetylene, the expected increase of efficiency and of wave length was found with increasing number of conjugated π electrons. In the series of diphenylpolyenes, $C_6H_5(CH=CH)_nC_6H_5$, the efficiency reached a maximum for $n=2$; with larger molecules self-quenching played an increasingly important role. Koski (29) also studied fluorescence of plastics containing a small percentage of anthracene or stilbene in solution. Aliphatic plastics such

as lucite give little or no fluorescence, but solutions in polystyrene proved almost as efficient as crystals of anthracene or stilbene. The polystyrene itself shows fluorescence at short wave lengths, but the addition of anthracene shifts the wave lengths to the region characteristic of anthracene. Energy absorbed by the plastic is transmitted to the anthracene or stilbene either by absorption of photons emitted by the plastic or by migration of the excitation. The transfer of energy in glassy solutions containing anthracene and naphthacene was studied by Moodie & Reid (30) using ultraviolet light rather than high energy rays as source of excitation. Wave lengths absorbed only by anthracene caused fluorescence of naphthacene. The naphthacene fluorescence was greatly enhanced when this compound was present as microcrystals rather than in true solution. This effect may be due to adsorption of anthracene on the aggregates of naphthacene.

Considerable work has appeared recently on liquid scintillation counters for γ -radiation. They are used in much the same way as the anthracene crystals except that the phosphor is a solution of some fluorescent material like stilbene in an aromatic solvent such as xylene. Energy absorbed by the solvent is transmitted with high efficiency to the dissolved phosphor when the concentration of the phosphor is less than 1 per cent. These counters are of particular interest to radiation chemists in demonstrating that excitation energy can be transferred through many molecules of liquid without degradation. The liquid scintillation counters have been recommended for detection of fast neutrons (31). Like anthracene crystals, they show a much smaller light output per unit energy input for α -rays than for γ -rays or fast electrons (32). The fluorescence in these solutions is readily quenched by addition of most foreign materials. Colgate (33) attempted to increase the efficiency of the solutions for γ counting by adding materials of high density to increase the energy absorption. Many materials were tested, including diphenylmercury, iodobenzene, and lead stearate. All unfortunately quenched the fluorescence. Kallmann (34) has made a very thorough study of these counters. For a variety of solutions the relation between the light yield, I , and the concentration, C , shows a maximum at a certain value of C and the relation follows the equation $I \sim PC/(Q+C)(R+C)$. Of the three constants in the equation, one is considered to measure the energy transfer from solvent to solute, one the internal quenching or dissipation of energy within the solute molecule, and one the self-quenching or loss of excitation through the interaction between solute molecules. More explicitly, if t_s is the mean life of activated solute for light emission, t_i the mean life of the activated solute for internal quenching, t_q the mean life against quenching for an activated solvent molecule, α the probability of energy transfer from solvent to solute, β the probability of self-quenching and n_s the rate of excitation of the solvent, then

$$P = n_s/\beta t_s, \quad Q = 1/\alpha t_q, \quad \text{and} \quad R = (1 + t_s/t_i)/\beta t_s.$$

Numerical data are given for various systems.

Kallman & Furst (35) have given data for practical light output obtain-

able from numerous combinations of solvents and solutes, both good and bad. In general the relative efficiency of the series of solutes did not vary greatly in different solvents, and the relative efficiency of different solvents was comparable with different solutes. It is rather surprising that addition of nonhydrocarbon substituents to the compounds often improved the results. The best solutes were anthranilic acid, diphenylhexatriene, α -naphthyl amine, phenyl- α -naphthyl amine, and terphenyl. The best solvents, surprisingly, were phenylcyclohexane and diphenyl ether; other good solvents included such expected liquids as benzene, toluene, and cumene but also tetrahydronaphthalene, phenetole and, most surprisingly *p*-dioxane, which is not an aromatic compound at all. A more detailed study of some of these systems could give results of the greatest interest to chemists.

Chemical reactions occurring on irradiation of simple aromatics have been studied in some detail by Burton *et al.* (36), Hentz & Burton (37) and Sworski *et al.* (38). The photolysis by ultraviolet light of liquid and vapor and radiolysis by fast electrons of liquid were studied for toluene, mesitylene, ethyl benzene, isopropylbenzene, and tertiary butyl benzene. In the photolyses the quantum yields for gas production are extremely small, of the order of 10^{-4} , both in liquid and in vapor. The 100 ev yields, G , for the radiolysis are of the order of .2 for gas production. This value is somewhat smaller than might be expected for the compounds with several substituent carbon atoms, and it is suggested that energy originally imparted to the aliphatic part of the molecule migrates in large part to the ring where it is dissipated with little chemical effect; this is described as "sponge-type protection." Detailed data are given for the relative yields of hydrogen, methane, and higher hydrocarbons in the reactions. Hydrogen is the chief product in all the liquid phase photolyses, but in the vapor phase photolysis of the ethyl, isopropyl, and tertiary butyl compounds, methane and higher hydrocarbons are more prominent. The liquid phase radiolysis of these same compounds also gives a considerable percentage of hydrocarbons in the gas. How to interpret the results in detail is not yet apparent, although it seems probable that excitation of the π electrons in the ring is the chief source of chemical action even in the radiolysis of the more highly substituted compounds. Sworski & Burton (39) have produced radiolysis of toluene by electrons and by the mixed fast neutron and γ radiation of the Oak Ridge nuclear reactor. The fast neutron source gave a lower ratio of methane to other gaseous products than the electrons. This is interesting as it is the first case in which an ionization density effect has been determined with precision for an organic compound. Manion & Burton (40) irradiated mixtures of benzene and cyclohexane, benzene and toluene, and cyclohexane and cyclohexene with fast electrons. The yields in the mixtures were less than those expected if each compound had been reacting independently. Benzene protects the other molecules against radiation decomposition. The result may be brought about both by transfer of excitation or ionization from the other component to the benzene as well as by changing the nature of reactions of free radicals which may be occurring in these liquids.

OTHER ORGANIC MATERIALS

Organic materials when irradiated invariably display a variety of reactions leading to a mixture of compounds extremely difficult to analyze completely. Characterization of all these reactions is nevertheless necessary to any understanding of reaction mechanisms. A detailed study of products from the irradiation of fatty acids was carried on at Massachusetts Institute of Technology over a long period. Some salient results have been summarized in a recent paper by Whitehead, Goodman & Breger (41). The main reactions are decarboxylation, $\text{RCOOH} \rightarrow \text{CO}_2 + \text{RH}$, and other reactions yielding H_2O , CO , and H_2 . Numerous acids were studied with the number of carbon atoms ranging from 2 to 30. The ratio of hydrocarbon to the sum of CO_2 , CO and H_2O in the products is constant for all of these acids and equal to 0.37. The absolute yield of hydrogen reaches a maximum at C_{16} , but the ratio of the H_2 to the CO_2 , CO , and H_2O continues to increase as the number of carbon atoms increases, since the total yield falls for the larger molecules. Temperature changes affect the yield slightly but this effect appears to be different for different acids. The data are good in quality and accuracy and monumental in quantity, and probably warrant a fuller discussion in terms of reaction mechanisms than the authors have offered. A similar detailed study of aliphatic alcohols has recently been offered by McDonell (42) working with A. S. Newton. The introduction to McDonell's report includes a fine review of the present status of the field of organic radiation chemistry. Cyclotron alphas were used to bombard alcohols ranging from methyl to decyl including two isomers of propanol and four isomers of butanol. Gaseous products were analyzed by mass spectroscopy, and liquid products were analyzed for water, carbonyl compounds, aldehydes, total glycols, and vicinal glycols. Although the products were complicated, the data show considerable restrictions on their nature. Except for CO , no product more than one oxidation state removed from the original alcohol is found in appreciable quantity, and many of those which would be allowed by this limitation are not found. The main reactions involve the groups attached directly to the COH group. The only glycols formed were the vicinal. The major products from the primary alcohols besides the glycols were hydrogen, water, and aldehyde. Secondary and tertiary alcohols give methane as an important product. A good material balance with respect to oxidized and reduced products is obtained from methanol but higher alcohols give some excess hydrogen for which no equivalent oxidized products could be found. The number of equivalents of reduction occurring per 100 ev input was about 7.5. Some excess water also appeared in some cases. Both dehydration and dehydrogenation are likely to yield unsaturated products which may polymerize and escape detection. With an increasing number of carbon atoms the yields of water, carbonyl compounds, and glycol fall off, and the nonfunctional tendencies increase. The tendency for the reaction to be located on the carbon holding the OH group is still striking, however, and it is now clear that radiation certainly does not break bonds indiscriminately, as appeared at one time, but acts as a reasonably selective reagent. It is not yet clear to

what extent such reactions are unimolecular decompositions which form molecules directly rather than by going through free radicals. That radicals do form in such reactions was shown by Williams & Gevantman (43) who irradiated alkyl iodides or saturated hydrocarbons in the presence of radioactive iodine. The iodine acts as a trap for free radicals, forming radioactive iodides which are separated by distillation after addition of quantities of inactive alkyl iodides to serve as carriers. Presence of a variety of radicals was demonstrated in this way and the method is a promising one for further study of organic reaction mechanisms.

Radiation readily causes polymerization of reactive monomers. Schmitz & Lawton (44) studied the polymerization of acrylates, methacrylates, styrene, and acrylonitrile by cathode rays. Difunctional monomers such as tetraethylene glycol dimethacrylate polymerized 50 times as fast as the monofunctional. The reactions are inhibited by oxygen or benzoquinone as expected for free radical reactions. From the magnitude of induction periods at low benzoquinone concentrations, an ion pair yield for chain initiation of about 3.0 was calculated.

The effect of radiation on plastics may be expected to be instructive as a comparison between liquid and solid phase reactions. Schneider, Day & Stein (45) have studied by microwaves the paramagnetic resonance of irradiated plastic. The resonance found corresponds to the g value for free electrons but is displaced 20 gauss as might be expected for a trapped electron. Polymethyl methacrylate containing dissolved dye gives negative centers of greater stability against both time and oxygen. It is interesting to find that these molecular compounds can trap electrons in much the same way as ionic solids. The resonance bands have a symmetrical structure attributed to interaction with magnetic dipoles in the polymer molecules, and the space between these dipoles and the electron may be calculated and agrees with x-ray data for both methyl methacrylate and polystyrene.

A much more practical approach to the subject of radiation effects on plastics is offered by Sisman & Bopp (46). They tested the physical properties of numerous plastics irradiated in the Oak Ridge nuclear reactor. In order of radiation resistance, beginning with the most resistant, they give: (a) mineral-filled furan and phenolics, (b) styrene polymers, (c) modified styrene, (d) aniline-formaldehyde and polyvinyl carbazone, (e) polyethylene and nylon, (f) mineral-filled polyester, (g) unfilled polyesters, (h) cellulosic-filled phenolic, (i) melamine-urea, (j) unfilled phenolic, (k) vinylidene chloride and vinyl chloride acetate, (l) cellulose and casein products, methyl methacrylate, teflon and fluorethene. The fluorocarbon plastics, which are the most resistant to heat and ordinary reagents thus stand up least well of all under irradiation. Groups (a), (b), and (c) presumably derive their radiation resistance from their aromatic character. Groups (f) to (j) are all cross-linked. The chlorine compounds evolve HCl. The different physical properties such as elastic modulus, tensile, shear and impact strengths change in different ways for different plastics, but failure ultimately occurs through crumbling. All plastics darken under irradiation but none show any pro-

nounced change in the electrical properties except when HCl is formed. The stabilizing effect of mineral filling against radiation damage is very pronounced and certainly deserves further consideration. Although change of state from liquid to solid has often been reported as having only a minor effect on radiation yields, the decomposition of bromoform by x-rays is reported to occur with a good yield in the liquid state but not in the solid state (47).

The extensive work of Pollard and his school on radiation deactivation of dry enzymes and viruses is relevant at this point. A summary of the main findings was presented early in the year (48). More detailed presentation of some of the results is given in later papers (49, 50). Deuteron beams were passed through dry preparations of various enzymes and viruses, and the effective cross section for destruction of the biological activity of the materials (deactivation) was determined. The observed cross section tended to fall off with increasing speed of the deuteron because faster deuterons may traverse some molecules without any loss of energy. The true cross sections are obtained by extrapolation to zero speed (infinite ionization density). Cross sections for the enzymes pepsin, trypsin and chymotrypsin correspond to molecular weights of 35,000, 24,500, and 16,500, respectively; the real molecular weights are all about 36,000. Thus it appears that whenever an ionization occurs within a pepsin molecule, the whole molecule is rendered inactive as far as its biological activity is concerned. The enzyme urease, however, showed a smaller cross section which did not vary in the expected way with ionization density, and in this case the deactivation apparently did not extend over the whole molecule. The inactivation by heat of the dry preparations was also studied, and it was shown that the heat due to the radiation acting on the molecule was not enough to deactivate it. An interesting correlation appears between large cross sections for ionization deactivation and high activation energies and large temperature-independent factors for rates of thermal deactivation. In both radiation and thermal deactivation the picture is presumably that a molecular unfolding, starting at one point, spreads spontaneously through the molecule. Preparations of T-1 bacteriophage show a small target size, and the virus is concluded to possess about 130 separate radiosensitive regions. Spores give higher cross sections than viruses. Fast electrons give target sizes comparable with the deuteron results if calculated on the basis that the average amount of energy transferred by the electron in the primary step is 115 ev, distributed at random through the material. In the case of catalase the situation is less clear (51). The cross section corresponds to a molecular weight about half that of the molecule but the temperature-independent factor in the thermal deactivation is small. A preparation partially inactivated by heat shows a much larger cross section for deuteron bombardment. Thus heat throws the molecule into a form which is abnormally radiosensitive but is still catalytically effective.

AQUEOUS SOLUTIONS

Aqueous solutions furnish the most popular subject for study in radia-

tion chemistry. The greater attraction lies first in the fact that the reactions are more clear-cut and the mechanisms better understood than in other fields of radiation chemistry, and second, in the continuing belief that aqueous solutions furnish the best approach to understanding the chemical mechanisms of the action of radiation on living things.

The mechanism of decomposition of water under the mixed fast neutron and γ radiation of the Oak Ridge reactor was studied by Allen, Hochanadel, Ghormley & Davis (52). The decomposition of water proceeds to a limited extent and then comes to a standstill because of back reaction. A significant result was that the rate of hydrogen production from a wide variety of solutions of simple inorganic compounds was the same. This rate was evidently characteristic of water decomposition, and it was clear that water under irradiation decomposes to give molecular products in a reaction which is unaffected by the presence of solute molecules. In pure water the molecular products are acted upon by free radicals, which are also formed by the radiation, and the products are reconverted to water. Addition of solutes protects the decomposition products by destroying the free radicals by oxidation-reduction reactions. The product accompanying hydrogen in the molecular decomposition was believed to be H_2O_2 , although some molecular oxygen may also be formed initially. The main initial chemical reactions occurring when aqueous solutions are irradiated are therefore:



The molecular reaction is believed to occur in regions of high density of energy release along the charged particle tracks; radicals formed in these regions can combine with each other before they have time to separate by diffusion. The H_2O_2 decomposes to oxygen in a secondary reaction. The back reaction, or combination of the reaction products to re-form water, is a rapid chain reaction believed to occur through the steps



Decomposition of H_2O_2 to O_2 can be explained by the reactions



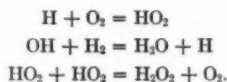
The decomposition of H_2O_2 is rather irreproducible in rate, and this appears characteristic of any system in which reactions of the radical HO_2 are rate determining. A study of the reaction in solutions containing H_2 and H_2O_2 showed that reproducible results could be found when the concentration of hydrogen was greater than twice the peroxide concentration. The mechanism here should presumably consist of equations 1, 2, 3, 4, 5, and 6, equation 7 being unimportant when hydrogen is in excess, since the excess hydrogen

keeps the concentration of H higher than that of OH because of the occurrence of reactions 3 and 4. This mechanism leads to the rate equation

$$-\frac{d(H_2)}{dt} = -\frac{d(H_2O_2)}{dt} = -k_2I + \frac{k_1Ik_4(H_2)}{k_3(H_2O_2)}$$

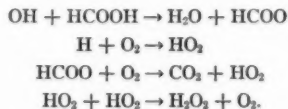
where t is time and I radiation intensity. The experiments showed complete agreement with this equation thus giving strong support to the theory. The back reaction is thus accelerated by high hydrogen concentration but inhibited by H_2O_2 , and this inhibition is also found with oxygen. It was found that water containing hydrogen did not decompose at all on irradiation, but solutions of H_2O_2 or O_2 decomposed to a much greater extent than pure water.

The experiments were repeated and extended by Hochanadel (53) with γ rays from a radioactive cobalt source. The same kinetics were found for the reaction of hydrogen with H_2O_2 . In addition, studies were made of the reactions occurring in solutions containing hydrogen and oxygen. When both gases are present, the only net reaction initially occurring is the formation of H_2O_2 with hydrogen and oxygen disappearing in equimolar amounts. As the hydrogen becomes depleted, decomposition of peroxide to oxygen and water begins to occur. The rate of formation of peroxide was independent of concentrations of H_2 and O_2 as long as both were present in reasonable concentration, and it was concluded that the main reactions occurring were



If this is the mechanism, it is possible to obtain a figure for the absolute rate of water decomposition to form radicals. Hochanadel concluded that under γ -radiation the yields of decomposition by reactions 1 and 2, were respectively 2.74 and 0.46 per 100 ev of energy absorption.

Studies by Hart (54, 55) on the mechanism of reactions of formic acid solutions under γ -radiation have led him to similar conclusions. Formic acid in solution decomposes to H_2 and CO_2 . On the addition of H_2O_2 a chain reaction with a high yield occurs leading to formation of CO_2 and H_2O by the equation $HCOOH + H_2O_2 \rightarrow CO_2 + 2H_2O$. In solutions of formic acid and oxygen, H_2O_2 is formed by the equation $HCOOH + O_2 \rightarrow CO_2 + H_2O_2$, and H_2O_2 does not react further with the formic acid until all the O_2 is used up. The yield of CO_2 is the same in solutions containing O_2 as in pure formic acid solutions, and the reaction mechanism in the O_2 systems is thought to be



On the basis of this system the hydrogen yield should decrease with increasing oxygen concentration and attain eventually a value characteristic of the

molecular decomposition of water (reaction 2). At high oxygen concentrations all hydrogen atoms and HCOO radicals will react readily with O_2 , and the CO_2 yield is equal to the total yield of free radicals (reaction 1). Hart's yield values for reactions 1 and 2 are 2.78 and 0.35, in good agreement with Hochanadel's values. Both values for the radical yield are based on the idea that HO_2 disappears only by reaction with itself, and if any HO_2 disappears otherwise the yield will have been underestimated. Hart (56) has also studied reactions of ferrous sulfate solutions, using β -rays from tritium as well as γ -rays as the radiation source. He points out that using the accepted reaction mechanism somewhat different values are obtained for the yields of reactions 1 and 2. The present author understands that extensive work by Weiss, to be published shortly, will lead to a revision of the ferrous sulfate mechanism. Other interesting reactions are under study in Hart's laboratory and the status of the investigations as of late 1951 is given in a recent report (57).

Johnson (58) has studied the decomposition of hydrogen peroxide in solution by high energy x-rays in the presence and absence of potassium iodide. The decomposition rate is high and varies with the square root of the initial peroxide concentration but is independent of radiation intensity at high intensities. Addition of potassium iodide increases the rate. The formation of hydrogen gas occurs at a rate independent of the rate of H_2O_2 decomposition or the amount of conversion of H_2O_2 to O_2 .

A group of investigators in France have been studying radiation chemistry of water and simple solutions with results which appear to be rather at variance with the results of the American groups. Bonet-Maury (59) has summarized his earlier publications on the formation of peroxide in air-free and aerated water under radiation by α -rays and x-rays. He explains the results by decomposition of water to H and OH radicals along the particle tracks, in agreement with the earlier accepted picture, which is not far different from the ideas of the American school. He has also made some observations on the effect of nuclear reactor radiation on water and solutions of boric acid (60). Lefort (61) made a thorough study of the decomposition of water by α -rays from radon. He finds that during a considerable period at the beginning of the reaction, the yields of H_2O_2 and O_2 are constant, indicating that both are formed initially in the decomposition of water. The 100-ev yields are: for H_2 , 1.8; for H_2O_2 , 0.94; for O_2 , 0.41. Decomposition of H_2O_2 to O_2 under α -rays is found to be much slower than with γ -rays, since relatively few radicals escape from the region of the α -particle track, where radical concentration is relatively very high. Lefort has studied the decomposition of H_2O_2 in solution by x-rays (62) and finds a constant small yield of H_2 to be formed, in agreement with Johnson (58). So far the results and interpretation are not in wide disagreement with others. In a paper by Haissinsky & Magat (63), however, a new interpretation is proposed, according to which an electron produced in water by radiation may react to form H_2+O^- , instead of the usually accepted reaction to give H and OH^- . The O^- is the basic form of the OH radical, and Haissinsky's view is that

nearly all the free radicals produced in water by radiation are OH, with H forming only rarely as a result of secondary reaction between OH and H₂. The radical OH is thought to behave as a reducing agent to strongly oxidizing solutes as well as an oxidizing agent; thus it might react with ceric ions by the equation $\text{OH} + \text{Ce}^{++++} + \text{H}_2\text{O} \rightarrow \text{Ce}^{+++} + \text{H}^+ + \text{H}_2\text{O}_2$. Extensive data on the reactions of ceric sulfate in acid solutions and ceric carbonate complex in alkaline solutions under x-rays were published by Haissinsky *et al.* (64) and Lefort & Haissinsky (65) and appeared to support Haissinsky's theory. High yields of molecular hydrogen were reported to form in the course of the reduction of ceric sulfate. Addition of O₂ was found to increase the yield for reduction in acid solution while addition of H₂ lowered the yield. The effect of hydrogen is explained by supposing that the OH radicals reduce the ceric sulfate directly, and hydrogen reacts with OH to form atomic hydrogen which is apparently a less efficient reducing agent. In the alkaline solutions, ceric ion is not reduced at all but cerous ions are completely oxidized to the ceric state. This work was all performed with soft x-rays of effective wave length 0.9 Å. The reduction of ceric sulfate by tritium β-rays was studied by Challenger & Rollefson (66) who report that the reaction was inhibited by the presence of cerous sulfate, a fact which is not reported by Lefort & Haissinsky (65). The results of the French workers on the ceric sulfate solutions are, however, entirely in disagreement with results obtained by Hardwick at Chalk River using γ-rays, which were published too late to be included in this review. It appears likely at this writing that there is a very large effect of wave-length of the radiation used on the kinetics of this reaction, and judgment on the reaction mechanism should be suspended until further data are obtained.

Dewhurst (67) has studied the increase in rate produced by small additions of alcohol in the γ-ray oxidation of aerated acid ferrous sulfate solutions. This effect was expected because of the large effect of alcohol on the thermal reaction between ferrous sulfate and H₂O₂, which is thought to have a similar mechanism to the radiation reaction. Addition of chloride ion suppressed the effect of alcohol on the radiation reaction.

A small amount of reduction of CO₂ in aqueous solution under bombardment by cyclotron radiation was reported by Garrison and co-workers (68). The ion pair yield (32.5 ev) for formic acid production was 2.8×10^{-6} in pure water, 3.4×10^{-4} in ferrous sulfate solution; the formaldehyde yield was zero in pure water, 8×10^{-3} in ferrous sulfate solution. The reaction is thought to have some bearing on the problem of how life originated in the primeval oceans.

Dainton (69, 70) has reviewed some of his work on kinetics of polymerization of acrylonitrile in aqueous solution. The results were discussed in the previous volume of *Annual Review of Physical Chemistry* (2).

Theoretical studies of the distribution of radicals along the track of a charged particle must serve as a guide in setting up the chemical reaction mechanisms. Gray (71) has again reviewed his picture of the distribution and behavior of radicals in water, according to which hydrogen atoms are formed

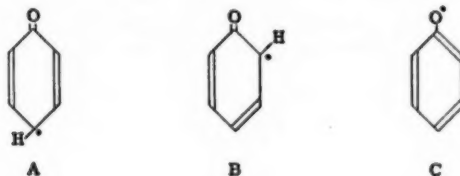
by electrons ejected from the track only after the electrons have diffused a considerable distance (of the order of 150 Å) so that an initial segregation of OH radicals and H atoms occurs. The radicals then diffuse outward, recombining all the time so that much of the action occurs within a track independently of what occurs in the body of the solution as a whole. The theory is greatly handicapped by the absence of any rigorous mathematical solution to the nonlinear differential equation which describes the process of combined diffusion and bimolecular recombination. Krenz (72) has given a treatment of this equation from which certain numerical results are obtained. The results appear to indicate a smaller rate of recombination of radicals during outward diffusion than had previously been supposed by Gray and by Dainton. Read (73) has considered the consequences of the supposed segregation of positive and negative ions along the track. Such segregation will produce powerful electric fields. Read calculates the equilibrium value for separation of the positive and negative charges under thermal agitation, but is apparently unable to arrive at a solution of the problem complete enough to be of definite value in radiation chemistry. The problem of the initial extent of segregation of the radicals and of the subsequent behavior in diffusion and recombination is still far from solution.

Dee & Richards (74) point out that another effect may be important in radiation chemistry of solutions, namely the production of photons in the radiation track which may be absorbed directly by solute molecules throughout the solution and thereby produce chemical reaction. In support of this idea they report experiments in which a solution of polonium, separated by a thin quartz window from another solution, produced chemical reactions in the other solution, which contained ferrous sulfate, sodium iodide, or chloroacetic acid. The extent of reaction was as much as 5 per cent of that obtained when the polonium was added directly to the reagent solution. The photon effect would seem to be quite important in the case of α -rays but it should be remembered that yields of indirect action with α -rays are much lower than with γ -rays, and the photon effect may well be of very minor importance in the γ -ray case.

Turning now to solutions of organic compounds, we find a summary by Minder (47) of a long series of experiments on formation of HCl in solutions of organic chlorides. The formation of HCl may be linear with dose or exponential according to the compound used. The decrease in yield with increased dilution was studied with special attention. The concentration at which the yield falls to $1/e$ of its high-concentration value was taken as a measure of the mean range of energy conduction through the water into the solute; this range varies from 54 to 214 Å for aqueous solutions of different chlorides. Although Minder agrees that the energy is transported through the solute by diffusion phenomena, as evidenced by the lack of action in frozen solutions, he believes that the activated water dies away unimolecularly, rather than by a bimolecular combination of radicals as had been previously proposed by several authors. One theory should lead to an exponential curve of yield versus concentration, while the other yields a hyperbolic curve, but the data are not sufficiently accurate to distinguish between

these functions. Studies in alcoholic solution gave similar results to those in aqueous solution, with the mean range of energy production being smaller, ranging from 24 to 40 Å. Extensive detailed data are presented on HCl formation in solutions of dichlorodiphenyltrichloroethane (DDT) in alcohol solution under x-rays. The addition of water up to 25 per cent to the alcoholic solution gave no effect on the HCl yield, which argues against a theory in which the reaction is determined by the specific chemical properties of free radicals. Minder seems to feel that the range of energy conduction in water is a fundamental physical property which is of great importance in determining the fundamental forms of biological systems.

An extensive series of researches on effects in solutions of organic compounds has been published by Weiss and co-workers. A review of the earlier results (75) mentions studies on solutions of benzene which under radiation produce phenol and diphenyl, the important reactions being $\text{OH} + \text{C}_6\text{H}_6 \rightarrow \text{H}_2\text{O} + \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_6 + \text{OH} \rightarrow \text{C}_6\text{H}_5\text{OH}$, $2\text{C}_6\text{H}_6 \rightarrow (\text{C}_6\text{H}_5)_2$. Nitrobenzene in solution gave *ortho*-, *meta*- and *para*-nitrophenols in approximately equal quantities, the ratio of these products depending somewhat on the pH. When ferrous sulfate was allowed to react with H_2O_2 in the presence of nitrobenzene, a similar ratio of the nitrophenol isomers was found indicating that the same free radical processes are at work in both cases. Solutions of phenol (76) under x-rays gave only the *ortho*- and *para*-dihydroxy benzenes with no *meta*- compound. In acid solutions the *ortho*-quinone was formed as a primary product in the presence of air but not the *para*-quinone. It was thought that the radical initially formed by the action of free OH on phenol could exist in forms as A, B, or C. Reaction of OH with forms A and B could



give rise to *ortho*- and *para*- compounds found; reaction with O_2 or HO_2 was thought to occur through the form C, yielding a peroxide which would react to give the *ortho*-quinone. Benzoic acid solutions (77) gave the *ortho*-, *meta*- and *para*-hydroxy benzoic acids in the ratio 5:2:10. Chlorobenzene (78) gave the *ortho*-, *meta*- and *para*-phenols in comparable amounts, both under x-rays and in the presence of ferrous sulfate reacting with H_2O_2 . In the presence of air the yield of chloride ion is considerable, but is greatly decreased in the absence of air, and the reaction is therefore an example of oxidative dechlorination. It would seem that Minder's picture of the reaction is greatly oversimplified.

Solutions of amino acids have presented a popular field of study owing to the belief that such reactions would shed some light on the problem of protein degradation by radiation. With many amino acids, an important

reaction is the formation of ammonia. This reaction according to Weiss (75) is chiefly a matter of oxidative deamination yielding CO_2 and aldehyde together with the ammonia, but some reductive deamination occurs presumably as a result of reaction with hydrogen atoms. Thus alanine solutions give acetaldehyde on irradiation in the absence of air (79) while in the presence of air further oxidation occurs to yield pyruvic acid. However, the pyruvic acid yield is independent of pH, while the yield of ammonia goes to a minimum near pH 7. Very small yields of hydroxylamine also appear in the irradiation of solutions of many amino acids (80) while ethylamine solutions also yield some hydroxylamine, but ammonium salt solutions yield only nitrite. Cystine, which contains a sulfhydryl group as well as an amino group, yields no ammonia but gives instead H_2S . According to Dale & Davies (81) the H_2S yield from cystine solutions under x-rays increases greatly as the concentration of cystine is increased and very high ion pair yields are found. The formation of H_2S has a maximum at pH 6. Glutathione gives similar yields of H_2S but the curve of yield versus pH has a double maximum. The cystine reaction was studied in greater detail by Rotheram, Todd & Whit-cher (82). They agree with Dale in finding extremely high ionic yields for the reaction at high concentrations. In addition to determining H_2S these authors also determined the yield of cystine formation and of cystine disappearance. The formation of H_2S is increased by deaeration, but the total yield of cystine disappearance is decreased. No valid explanation has been offered for the high yields observed. Dale (83) finds that the yield of ammonia from solutions of glycine and serine increases continually with increasing concentration, reaching values as high as 12 molecules of ammonia per 100 ev. Corson *et al.* (84) and Bhatia & Proctor (85) have studied the effect of cathode rays on solutions of *p*-aminobenzoic acid, anthranilic acid, and histidine. Concentration-dose curves were at least approximately exponential in these cases.

Allsopp (86) has reported very peculiar results in the irradiation of indole solutions by x-rays. The indole concentration was reported to rise and fall periodically with increasing dose. Effects were observed at doses as small as 1 r. Sometimes more indole appeared to be present after irradiation than in the original solution. One might suggest that different methods of analysis should be tried in this case. Weber & Schuler (87) have studied the decoloration of some dilute dye solutions. The reactions observed depended upon the presence of oxygen. The yield depends on the extent of reaction, the dye concentration, and the presence of acid or base, and the reaction is inhibited by thiourea and other protecting agents. Mead (88) has studied the chain reaction between oxygen and linoleic acid in aqueous solution under x-rays.

Solutions of sterols under x-rays show surprisingly specific reactions according to Weiss (75). Cholesterol gives hydroxylation of the double bond at the 5,6 position very cleanly with some attack also occurring at the 7 position, and pregnenolone reacts similarly. Cholic acid yields 7-ketodihydroxycholic acid (89). This reaction also occurs *in vivo* in certain metabolic processes, and Weiss believes that there is a general resemblance between

oxidations produced by free radicals and many biological oxidations.

The depolymerization of nucleic acid in solution under x-rays or ultraviolet rays has been known for some time. Smith & Butler (90) find that irradiation of a solution containing sodium thymonucleate and hydrogen peroxide with light of 3135 Å (which is absorbed only by the peroxide) shows depolymerization, and the kinetics are very similar to those given by x-rays on nucleate solutions. The implication is that OH radicals are the active depolymerization agents in both cases. Weiss (75) reports that nucleic acid not only depolymerizes under x-rays, but also gives ammonia, free purines, free inorganic phosphate, and shows an increase in titratable acid; the yield of ammonia decreases when oxygen is removed from the solution, and decreases further if hydrogen is added.

Dale (91) has reviewed his work on the protection of solutes against radiation damage by added materials. In some cases the efficiency of the protector decreases as the concentration of the protector is increased ("phenomenon of the changing quotient"). Smith & Butler (90) found that the nucleate in peroxide photolysis was protected against degradation by glucose and methyl alcohol in low concentrations but that the efficiency of these protectors decreased at concentrations over .05 *M*. With x-rays these protectors remained efficient to higher concentrations. If protectors act by reaction with OH radicals, then the product of this reaction must be a new radical which may act on the substrate somewhat less actively than the original OH radical. Apparently in no single case are the data sufficient for the complete treatment of the phenomenon to be worked out. The phenomenon of protection has also been discussed by Aten (92).

The mechanisms of biological action of radiation were discussed by Burton (93) from the viewpoint of radiation chemistry of solutions. Living things are composed of small aggregates of organic matter surrounded by water. Ionization in the organic material may eject an electron which is captured by the water. Energy may also be transferred from the organic molecules to the water by ionization transfer, since the ionization potential of liquid water may be lower than that of organic compounds. The effect on the water is to produce free radicals which may react with the organic material. The probability of an effective hit should therefore be highest near the boundary of an organic structure. Toulis (94) points out that many biological radiation effects are produced more efficiently by α -rays than by x-rays, although the free radical yield is certainly greater with the x-rays. He believes that the effects are largely due to molecular H_2O_2 , which is formed in greater amount by the α -rays.

Haissinsky & Gluzbarg (95) have studied the effect of γ -rays and neutrons on sols of copper (positively charged) and silver and gold (negatively charged). In agreement with some old results the negative sols were found to be stabilized by small radiation doses while the positive sol was destabilized. The stabilization of the negative sols is attributed to the reduction of OH radicals on the surface of the particle to form OH^- , which remains adsorbed on the surface.

Miller (96) finds that the action of ultrasonic waves on ferrous sulfate solutions is in many respects similar to the effects of γ -rays. However, unlike the radiation reaction, the sound reaction was suppressed completely by the addition of hydrogen or by warming to 50°C.

IONIC SOLIDS

On irradiation of simple ionic solids like the alkali halides, absorption bands appear which cause the crystal to become colored. A variety of bands may be produced which are known by various letters: F, F', V, R, M, N, L. Some of these bands form only as a result of secondary thermal reactions after the radiation. The bands are believed due to the trapping of electrons in various kinds of lattice imperfections and may be produced not only by radiation but by exposing crystals to the vapor of an alkali metal. The theory is discussed by Dexter & Heller (97), Seitz (98), and Dexter (99). A new type of bands at short wave-length, called α and β are discussed by Delbecq, Pringsheim & Yuster (100) and are ascribed to perturbation of the normal excitation levels of the crystal by the presence of trapped electrons. Electrons are released from the traps on warming or illumination as manifested by bleaching, thermoluminescence, conductivity, or photoelectric emission. Several experimental studies on these phenomena have appeared during the year (101 to 104). The "glow curves" obtained on warming irradiated crystals and plotting the light output versus temperature are very complicated due to the variety of traps existing (105, 106, 107). Daniels (107) finds that 75 per cent of natural rocks show thermoluminescence because of the irradiation they have received during geological time from the traces of radioactive material present. He suggests application of the effect in the correlation of strata, rough estimation of the age of rocks, and the detection of uranium in rocks. Thermoluminescence induced by γ -radiation may also find use, he suggests, in controlling the manufacture of crystals and in evaluation of catalyst preparations. Przibram (108) discusses the coloration observed in specimens of natural rock salt arising from radiation. Sheline, Sharp & Arner (109) believe that the coloration of glass under radiation is due to similar phenomena, but that the absorption bands are much broader. The whole subject is really a field of solid state physics rather than radiation chemistry, and a full treatment of this topic and the allied topic of the theory of phosphors is beyond the scope of this review.

With solids containing polyatomic ions, chemical reactions are observed under irradiation, but these chemical effects have received very little attention compared with the amount of work lavished on the physical effects produced in crystals of monatomic ions. Heal (110) reports that sodium perchlorate is decomposed by x-rays with a yield of six perchlorate ions disappearing per 100 ev energy input. The products consist of about one-fourth chloride, three-fourths chlorate, and small amounts of chlorite and hypochlorite. Chlorates also decompose under x-rays, but iodates do not. Solid potassium bromate appears to decompose under radiation as demonstrated

by Boyd, Cobble & Wexler (111) in the course of studies of the Szilard-Chalmers reaction in solid potassium bromate. The study of the radiation chemistry of solid salts would appear to be a promising field, since the physical situation is now fairly well understood.

CHEMICAL DOSIMETRY

Chemical dosimeters have the advantage over ionization measurements of giving a ready measure of the total dose received by an object without special apparatus and without the necessity of integrating a dose rate over a period of time. Chemical dosimeters are also applicable to the region of high doses to which the electrical instruments are not so well suited. Problems of chemical dosimeters are discussed by Day & Stein (112), and their benzoic acid dosimeter is described in detail. The product in the irradiation of benzoic acid solution consists of a mixture of hydroxylated acids, and determination of these acids by the colorimetric method indicated by Day & Stein appears to give somewhat equivocal results. Carr (113) finds that a determination of phenols in the irradiated solution by light absorption at $270\text{ m}\mu$ is more reproducible but less sensitive than the chemical test. Day & Stein (112) also recommend deaerated agar gels containing methylene blue or other dyes which are bleached by radiation to obtain a picture of the geometry of the dose field around an x-ray source. The dye bleaching is a reductive process and is believed to result from hydrogen atoms; addition of benzoate to the gel increases the yield of bleaching, presumably because of reaction of benzoate with OH radicals.

Taplin & Douglas are continuing work on their chloroform-water dosimeter. An acid-base indicator (bromocresol purple) is dissolved in the water and changes color when radiation releases HCl from the chloroform (114). The most recent report (115) shows that by purification of the chloroform the system can be made sensitive to doses as small as 1 r. The system is, however, somewhat temperature sensitive and surprisingly dependent upon wave length, the amount of acid per roentgen being doubled in going from wave lengths of 0.015 \AA to 0.26 \AA . The sensitivity depends upon the amount of dye added. A certain amount of acid will suffice to change the color of the dye and further irradiation will not be shown. Kanwisher (116) prefers to determine the HCl in this system by a radiofrequency bridge (Q-meter). Films of polyvinyl chloride containing methyl violet are recommended for dosimetry by Henley & Miller (117). The dye changes color when HCl is produced by radiation in the plastic. This system is very insensitive and may be used up to doses as large as 10^{10} r. The color change is not a simple function of the dose. Day & Stein (118) report that methyl methacrylate plastic containing an azo dye deepens in color on radiation because of trapping of electrons by dye molecules and that the depth of color is proportional to the dose in the absence of oxygen and may be used as a dosimeter.

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currently exists as to the absolute value of the yield. Careful calorimetric and ion-chamber measurements by Hochanadel (53) showed that the yield was 15.5 molecules of ferrous sulfate oxidized per 100 ev energy input, in contrast to the previously accepted value of 20.6. The discrepancy is serious, since practically all the basic data in the radiation chemistry of aqueous solutions are obtained via this actinometer. Further work by various methods is urgently required to clear up this discrepancy.

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POLYMERIC ELECTROLYTES¹

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Polymeric electrolytes, commonly called polyelectrolytes, are at class of high polymer molecules having ionizable groups as part of their repeating unit. Thus the unique properties of high polymers are wedded to those of electrolytes in a single molecule. Against the background of the now classical theory of electrolytes and of the more recently consolidated understanding of polymer molecules, the exploration of the properties of polymeric electrolytes and the formulation of a theory of their behavior is in order.

The earliest investigations of polyelectrolytes are recorded in the books of Pauli & Valko (1) and Staudinger (2). The recognition of the marked increase of the reduced viscosity, η_{sp}/c , of polyelectrolyte solutions upon dilution, and the elimination of this effect upon the addition of salts, was the most valuable result of this early work. Following this, several studies on inadequately characterized natural polyelectrolytes, e.g., that of Briggs (3), showed that the apparent dissociation constant of a weak polymeric acid decreased with neutralization and dilution, and suggested that the conductivity of such solutions was due principally to hydrogen ions. In 1938 the systematic investigation of the physical chemistry of polyelectrolytes was initiated in the first of a series of important papers by Kern (4, 5). This review is particularly concerned with the work since that time.

In surveying this area one is continually aware of the dependence of progress here on advances in related fields and, conversely, of the contribution which the proper development of polyelectrolytes will make in these related fields. Since these interrelations cannot be developed here, specific mention may be made of: (a) the electrochemistry of proteins in which the effects of electrostatic interaction of charged groups and the behavior of rigid polyampholytes has been clarified (6), (b) the investigation of ion-exchange resins, produced by densely cross-linking polyelectrolytes, which was reviewed in the previous volume of this series (7), and (c) the recent theoretical investigations of the interaction and electrokinetic behavior of charged colloidal particles (8, 9).

Returning to the more limited problem of the physical chemistry of polyelectrolytes, we note the considerable diversity to be expected in these substances. On the electrolyte side there are weak polyelectrolytes, generally acids or bases, whose dissociation is of particular interest. Upon neutralization, salts are produced which are strong electrolytes. Alternatively, strong

¹ The survey of the literature pertaining to this review was concluded in February, 1952.

polyelectrolytes whose ionization is not dictated by pH and which are indeed soluble in a variety of organic solvents can be readily synthesized. In addition, long chain polymers carrying both acid and base groups—polyampholytes—can be prepared synthetically or from numerous biological sources. For polyelectrolytes as for other macromolecules, the common variables: molecular weight, molecular weight distribution, compositional heterogeneity, and branching, may be expected to play a significant role. Provided the structure is known, however, there is little reason to differentiate formally between synthetic and natural polyelectrolytes; the former can frequently be tailor-made to the specifications of a given experiment, the latter are often of more intrinsic interest.

THE TITRATION OF POLYELECTROLYTES

Polyacids.—The reactions of polyelectrolytes with either acid or base properly fall into the general category of equilibrium phenomena, which are dealt with later in this review; the discussion of the titration of weak polyelectrolytes has been set apart, however, because the acid-base behavior has been extensively investigated, both in theory and experiment, and offers a lucid picture of the specific effects brought about by the interaction of a large number of charged groups.

To emphasize these particular effects, let us recall briefly some pertinent characteristics of weak electrolytes in aqueous solution. The behavior of a weak, monobasic acid, such as, for example, acetic acid in dilute solution, for which activity corrections are negligible, is defined by the equations

$$K = \frac{[A^-][H^+]}{[HA]} = \frac{[H^+]\alpha}{1 - \alpha} \quad 1.$$

$$\alpha = \frac{[A^-]}{c_n} = \frac{K}{[H^+] + K} \quad 2.$$

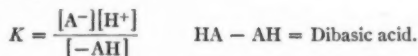
where K is the ionization constant of the acid, α the degree of ionization of the carboxyl groups, c_n the concentration of acid in equivalents per liter, and the bracketed quantities are the concentrations of the species in question. Two points are worth noting. (a) Knowledge of the dissociation constant K permits the calculation of the pH at any degree of ionization. (b) To the degree of approximation imposed by our neglect of the activity coefficients, the hydrogen ion activity, or the pH, is dependent only upon the degree of ionization, and not upon the equivalent concentration of the acid.

For a dibasic acid, the hydrogen ion activity in solution is determined by the relations for the two dissociation steps

$$K_1 = \frac{[HA^-][H^+]}{[H_2A]} \quad K_2 = \frac{[A^-][H^+]}{[HA^-]} \quad 3.$$

$$\text{and} \quad \alpha = \frac{[HA^-] + 2[A^-]}{C_n} = \frac{1}{2} \left\{ \frac{\frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}} \right\}. \quad 4.$$

For a hypothetical dibasic acid in which interactions between the ionizable groups are negligible, K_1/K_2 , the ratio of the two dissociation constants, should equal four (10). This is merely a consequence of the fact that as we fix our attention upon any given molecule of the undissociated dibasic acid in solution, the number of ways of removing a proton is twice that for a monobasic acid; however, for a molecule with one group ionized already, a proton can be removed in only one way, yet it can be affixed to the completely ionized molecule in two ways. Thus the first dissociation constant is twice the intrinsic constant (K_0) for the ionizable group and the second dissociation constant just one half of K_0 . Evidently the dissociation behavior of such a dibasic acid could as well be represented by a single dissociation constant, K , which specifies the ionization of the individual groups according to the equation



That our simple picture of two independent groups on a molecule is inadequate to represent the actual physical situation is evident from the stepwise ionization observed for most dibasic acids. In general, it is found that the ratio of the experimentally determined dissociation constants is larger than four; e.g., for malonic acid, $K_1/K_2 = 734$, for glutaric acid 11.9, and for pimelic acid 8.70 (11). It was Bjerrum (12) who suggested that in order to treat the electrostatic interaction quantitatively, the ionization be separated into two distinct steps—the removal of a proton from the ionizable group, with a free energy change equal to that of the ionization of the same group in the absence of any electric field, and the displacement of the proton to infinity against the field of the charges on the molecule, with a free energy change ΔF_e . The relation between dissociation constants becomes

$$K = K_0 \exp(-\Delta F_e/RT) \quad 6.$$

$$K_1 = 4K_2 \exp(\Delta F_e/RT) = 4K_2 \exp(-e\psi/D_e RT) \quad 7.$$

where e is the electronic charge, ψ the potential at the point of ionization, and D_e the effective dielectric constant; a knowledge of the electric field and the intrinsic dissociation constant thus suffices for the calculation of the titration curves. Interprotonic distances in dibasic acids evaluated from equation 7, using the dielectric constant predicted by Kirkwood & Westheimer (13), were found to be in satisfactory agreement with the values calculated from known bond lengths and valence angles (14). The study of such interactions was extended to the benzene carboxylic acids by Maxwell & Partington (15); the next systematic effort to ascertain the effects of the electric field of charged groups upon ionization was undertaken by Kern, who examined the titration behavior of high molecular weight polyacrylic acid, hereafter denoted as PAA (4).

The equations for the stepwise ionization of a dibasic acid can be generalized to give, for the case of a polyacid with p dissociable groups (16)

$$\begin{aligned}
 K_1 &= \frac{[H_{p-1}A][H^+]}{[H_pA]} \\
 &\vdots \\
 K_h &= \frac{[H_{p-h}A][H^+]}{[H_{p-h+1}A]} \\
 &\vdots \\
 K_p &= \frac{[A][H^+]}{[HA]}
 \end{aligned} \tag{8}$$

$$\alpha = \frac{\sum_h h[H_{p-h}A]}{c_n} = \frac{\sum_{h=0}^p \frac{h}{[H^+]^h} \prod_i K_i}{\sum_{h=0}^p \frac{1}{[H^+]^h} \prod_i K_i} \tag{9}$$

The usefulness of such a formalism depends, of course, on our ability to determine the individual constants experimentally; when p is of the order of a thousand, this approach obviously fails. However, if the interactions of the groups can be neglected, the behavior of a polyacid can be characterized by a single dissociation constant for the ionizing groups in the molecule. For this idealized case, the pK should be constant and independent of the degree of ionization; moreover, it follows from equation 1 that a plot of pH against $\log \alpha/1-\alpha$ should be linear with a slope of unity.

In experiments on samples of polyacrylic acid (PAA) of degree of polymerization 50 and 340, Kern (4) found that at a fixed extent of ionization and at a fixed equivalent concentration of the acid, the pH of the solution was independent of the molecular weight of the sample. However, the pK , as defined by equation 5 was not constant, increasing with increasing degree of dissociation. In spite of this, the pH of the solutions was linear in $\log \alpha/(1-\alpha)$, however, with a slope of two, instead of unity as would be expected if the assumption of absence of interaction between ionized groups were justified. To describe the behavior of the polyacid, Kern (17) proposed the relation

$$\alpha = \frac{1}{1 + \left(\frac{[H^+]}{K_m}\right)^{1-A}} \quad 0 < 1-A \leq 2 \tag{10}$$

in which $(1-A)$ is an empirical titration exponent, and K_m is the "median titration constant." Transposed, and in modern symbolism, this is equivalent to

$$\text{pH} = \text{p}K_m + n \log \frac{\alpha}{1-\alpha} \quad n = 1/(1-A). \tag{11}$$

At an equivalent concentration of 0.065 N , PAA yields the values $\text{p}K_m = 6.3$ and $n = 2$. Since in the absence of base the hydrogen ion concentration is $[H^+] = \alpha c_n$, equation 11 predicts a pH dependence on concentration given by

$$\text{pH} = \frac{1}{n+1} \text{p}K_m - \frac{n}{n+1} \log c_n \quad \text{for } \alpha \ll 1. \tag{12}$$

The experimentally observed plot of pH against $\log c_n$ for pure PAA obeys this equation (4), the values of n and pK_m agreeing well with those obtained from the titration data. However, it was observed that upon lowering the concentration of PAA, the pK_m value increased, necessitating an extrapolation to infinite dilution in order to obtain an unequivocal value for this constant (17). That pK_m as well as n depends on the valence of the cation introduced was established by titration with tetramethylethylenediamine instead of sodium hydroxide, resulting in a decrease of both parameters (17).

Kern found that relation 11 was valid for polymethacrylic acid (PMA), as well as a number of naturally occurring polyacids, such as gum arabic, agar, and various samples of nucleic acid (17). From his experiments, he tentatively concluded that n was an index of the intramolecular electrostatic interaction, being dependent upon the separation between ionized groups, whereas the pK_m played somewhat the same role as the dissociation constant of a monobasic acid (17). Before considering the validity of this point of view, it is instructive to compare the behavior of polyacids with that found for simple carboxylic acids. For acetic acid, $pK_m = 4.76$ and $n = 1$; in the region of half neutralization, the pH of such dibasic acids as adipic and pimelic is well represented by equation 11 using $pK_m = 4.95$ and $n = 1.2$. The increase in both these constants upon increasing the number of ionizable groups appears to reflect the increase in the charge density and hence the importance of electrostatic interactions. It can be shown that n is directly related to the deviation of the charge on the individual molecules from the average charge by the equation

$$n = \frac{p\alpha(1-\alpha)}{(h-\bar{h})^2} \quad h = \text{number of ionized groups per molecule.} \quad 13.$$

As the work required to remove a proton from the field of the groups already ionized is increased, the charge fluctuations must necessarily decrease, resulting in a higher value for n . To calculate the electrostatic contribution to this free energy of ionization, one must, of course, assume a suitable model for the molecular system. For proteins, the electrostatic field has been evaluated by assuming a smooth spherical distribution of charge; for thread-like molecules, such as PMA, the problem is much more complicated, since it involves the calculation of the effects of the charged groups upon the dimensions of the molecule. Several attempts in this direction have been undertaken, and the results will be summarized in the last section.

Let us consider now the dependence of pK_m and n values in typical polyacids on concentration, ionic strength, and structure. The lack of dependence of the pH on the molecular weight of the sample was verified for PMA by Katchalsky & Spitnik (18) and Arnold & Overbeek (19); the former investigators independently arrived at the simple empirical relation between pH and $\log \alpha/(1-\alpha)$ already proposed by Kern (17), and extended their investigation to a study of the effects of added salt and variation of dielectric constant on titration behavior. As could be expected from Kern's data on titration with divalent cations, addition of NaCl reduced both pK and n ,

the values changing from 6.5 and 2, without any salt, to 5.25 and 1.52 in .8 *N* NaCl. This same behavior was observed by Arnold & Overbeek for PMA (19), and by Kagawa & Katsuura (20) for carboxymethylcellulose. Titration of PMA in water-dioxane mixtures gave curves in which the pK_m increased with lowering of the dielectric constant, that is, under conditions leading to an enhancement of electrostatic interactions. As the dielectric constant of the titration medium was decreased, however, the value of n likewise dropped. To account for this, Katchalsky & Spitnik (18) suggested the necessity of an activity correction to the titration equation, giving the relation

$$pH = pK_m + n \log \alpha / (1 - \alpha) - \sqrt{\lambda c_c} \quad 14.$$

in which λ is an empirical activity correction factor and c_c the counter ion concentration. The values of λ calculated on the assumption of constant n were inversely proportional to $D^{3/2}$, as is predicted by the Debye-Hückel theory for the negative log of the activity coefficient. Katchalsky also found that this equation accommodated the concentration dependence of the pH, already observed by Kern. On the basis of titrations of PMA in very dilute solutions ($c_n = .025$ to $.0016$ *N*), Oth & Doty (21) proposed a correction term of the form $\sqrt{c}/(1 + \sqrt{c})$, which gave better agreement with their results than the simple square root dependence.

The effect of increasing the separation of ionizable groups along the polymer backbone upon the constants in the titration equation can be deduced from data of Johanson (22), Kagawa, (20), Speiser *et al.* (23), and Schultz *et al.* (24). Johanson studied the titration of a series of copolymers of crotonic acid with varying amounts of vinyl acetate, in 50 per cent water-alcohol mixtures; as the distance between carboxyl groups decreased, the pK_m value increased approximately as the cube root of the separation, and n decreased. Kagawa & Katsuura investigated the behavior of carboxymethylcellulose as a function of the number of carboxyl groups per glucose unit. Here again the pK_m increased with increasing density of ionizable groups; moreover, the values of n showed the same trend on increasing the degree of etherification. Kagawa's data on the effect of added salt reflects the decrease in the two constants to be expected from Katchalsky's work (18); titration of CMC with mixtures of sodium and barium hydroxide resulted in a decrease in pK_m and n on substitution of the divalent cation for sodium. These investigators also observed the dependence of pH on concentration and proposed the relation

$$pH = \frac{1}{2} \{ pk_s + l \log [\alpha / (1 - \alpha)] - \log c_n (1 - \alpha) \} \quad 15.$$

l being a titration exponent, and k_s a measure of the dissociation of the polyacid. This equation seems to represent the data of the authors adequately, but because of the logarithmic dependence of pH on concentration it can only be valid over a limited concentration range.

From the data of Speiser, Hills & Eddy (23) it appears that the titration of pectin, with 10 per cent of the available carboxyl groups esterified, can be

described by equation 11 with $pK_m = 4.2$ and $n = 1.7$. Upon increasing the number of esterified carboxyl groups, and therefore also decreasing the density of charge centers, the pK_m was lowered. Moreover, Schultz & co-workers (24) found that at the same degree of esterification, pectic acid in which carboxyl groups had been liberated by alkaline hydrolysis of the ester groups originally present, showed a lower pK_m than pectins subjected to enzymatic deesterification. Since the action of the enzyme is supposed to result in a nonrandom distribution of ionizable groups, in which several carboxyls may be at close intervals to one another, stronger interaction between the ionized groups would be expected for such a sample (25).

The particularly strong interactions of closely spaced carboxyl groups are also revealed in the titration of the so-called polydicarboxylic acids, prepared by copolymerization of maleic anhydride with a second vinyl monomer, such as, for example, styrene. The work of Garrett & Guile (26), and Ferry *et al.* (27) showed that the titration curve of such a material resembles that of a dibasic acid, in that there are two separate and distinct sections, the first of which can be represented by equation (11) with $pK_m = 4.40$ and $n = 1$. For the dissociation of the second carboxyl groups of the maleic acid residues which must occur against the field of the carboxyl groups ionized already, these constants assume the values 10 and 2, respectively. It is interesting to note that for copolymers of maleic acid and vinyl ethyl ether the two parts of the titration curve are not as clearly defined, indicating that the shielding of adjacent ionized carboxyl groups is apparently less effective.

On the basis of the evidence presented it is clear that both parameters of the Kern-Katchalsky equation are required to determine the effects of electrostatic interactions between ionizable groups. As already pointed out by Katchalsky (18), a generalization of this simple equation to

$$pH = pK + n \log [\alpha/(1 - \alpha)] + \lambda f(c_e) \quad 16.$$

f being a function of the concentration of counterions, and λ an activity correction factor, is needed to account for the variation of pH with concentration and ionic strength. At present, the experimental evidence does not permit an unequivocal assignment of the functional dependence of either λ or f , but it is evident that even for solutions infinitely dilute with respect to polymer, f must remain finite if pK is to be a constant characteristic of the dissociating group. This is only a consequence of the fact that for a poly-electrolyte a solution of noninteracting, ionized groups is possible only in the limit as both c and α approach zero. Even at infinite dilution, electrostatic effects which cannot be characterized by the constant n alone must manifest themselves, since at half neutralization the term $n \log [\alpha/(1 - \alpha)]$ vanishes. It must be emphasized that equation 11 is strictly empirical; actually it follows from equation 6 that the correction for the electrostatic contribution to the free energy of ionization should be additive, giving the equation (28, 29)

$$pH = pK_0 + \log [\alpha/(1 - \alpha)] + 0.434\Delta F_e/RT. \quad 17.$$

Since log-log plots are quite insensitive, it is possible to approximate this expression with the Kern-Katchalsky relation, and thus introduce a very significant simplification in the empirical characterization of electrostatic interaction in the acid base behavior of polyacids.

Polybases and polyampholytes.—No detailed investigation of the titration of polybases has yet been carried out, but the data on the variation of the pH of polyethylene imine with concentration, studied by Kern & Brenneisen (30), did fit equation 12; here, however, the pH decreased with decreasing molecular weight. This effect may have been caused by impurities which could not be removed from these low molecular weight preparations [degree of polymerization 27 to 51]. The data available on the titration of polyvinylpyridine (31) is limited because of the very small basic dissociation constant of this polymer and its insolubility in pure water.

Quantitative investigations of the physical chemistry of synthetic polyampholytes are likewise few. Wagner & Long (32) have carried out titrations of a copolymer of acrylic acid and 2-vinylpyridine; at the isoelectric point, this polymer is insoluble in distilled water, so that titration in this region cannot yield information of thermodynamic validity. As in polydicarboxylic acids, however, the titration curve falls into two distinct segments, each of which obeys the Kern-Katchalsky relation. From the similarity of the acid titration to that of polyvinylpyridine and that in base with PAA, Wagner & Long conclude that at the isoelectric point the polyampholyte exists as a neutral molecule rather than as a dipolar ion. This interpretation agrees with that of Alfrey & Morawetz (33), who investigated 2-vinylpyridine-methacrylic acid copolymers. It is, however, in conflict with the findings of Katchalsky & Miller (34), who reported, on the basis of a spectrophotometric study of a similar copolymer, that at the isoelectric point half the pyridine groups were ionized. Investigation of the titration of completely soluble polyampholytes, such as the one described by Alfrey *et al.* (35) and by Doty & Ehrlich (36), should be particularly fruitful in elucidating the effects of interaction of oppositely charged groups on the free energy of ionization, and permit comparison with the large body of information available from experiments on the titration of proteins.

TRANSPORT PROPERTIES

CONDUCTIVITY

Weak polyelectrolytes.—Weak polyelectrolytes, like weak electrolytes of low molecular weight, are generally acids or bases. Inasmuch as the conductance of weak electrolytes is the sum of the ionic conductances, and therefore accurately reflects the degree of ionization, conductance measurements on weak polyelectrolytes may be expected to provide similar information. Kern has investigated the conductivity of aqueous solutions of polyacrylic acid (4) and polyethylene imine (30) and compared them with their monomeric counterparts. With polyacrylic acid the equivalent conductance, Λ , (concentration being measured in equivalents per liter) is found to be insensi-

tive to the degree of polymerization.² At high concentration the polyacid conducts somewhat more than isobutyric acid but upon dilution the conductance of the polyacid falls below that of the isobutyric acid. Similarly the pH decreases less upon dilution than does that of isobutyric acid. Indeed Λ of the polyacid is matched very closely by attributing all of the conductance to the hydrogen ions. This leads to the tentative conclusion that polyion, which is here only about 1 per cent charged, does not participate in the conductance. The slower increase in Λ upon dilution for the polyacid is thus the result of the ionization step's producing only one current carrier rather than two as in the isobutyric acid. This same behavior, as judged by the agreement between pH calculated from the conductance of a polyacid and that measured, has been found in other weak polyelectrolytes, for example, in a maleic acid-styrene copolymer (37) and in pectin, i.e., pectinic acid (38). In the latter case, however, the observed conductance falls somewhat below that ascribable to hydrogen ions. Perhaps this is due to small errors in the pH measurement.

Salts of weak electrolytes.—Upon neutralizing weak polyacids of polybases, polysalts are formed which are strong polyelectrolytes. Kern (4) has shown that Λ of partially neutralized polyacrylic acid is independent of molecular weight, indicating that the mobility of the cation is unaffected by large changes in the solution viscosity. The mobility of the polyion at this degree of neutralization ($\alpha=0.54$) was calculated from the Λ of similar solutions in which Na^+ was replaced by Li^+ and K^+ assuming independent ionic mobilities. The result was 22.3, which, when compared with that for Na^+ of 50, indicates that the highly charged polyion, in contrast to the slightly charged one in the polyacid solution, is conducting. In analyzing his data on the dependence of specific conductance on the degree of neutralization, Kern assumed a zero mobility for the polyion. Using this assumption the specific conductance, above $\alpha=0.3$, is found to fall below that expected for the Na^+ ions alone. It would appear that this is due to association of Na^+ with the polyions beginning at $\alpha=0.3$ and increasing with α . The quantitative evaluation of counter ion association was not forthcoming until transference numbers were measured with the aid of radioactive tracers, as summarized in the next section. It is also possible to estimate the extent of association from conductance measurements by combining them with viscosity measurements using the assumption that the association vanishes at low values of α (21). Using polymethacrylic acid data that had been extrapolated to infinite dilution, it was shown that association began at about $\alpha=0.4$ and reached a total of 40 per cent of the Na^+ present at complete neutralization. Thus upon neutralizing a polyacid the majority of the cations added after $\alpha=0.4$ become, in effect, bound to the polyions. At infinite dilution the completely neutralized PMA appears to have $\Lambda_0=58$. The Na^+ contribution to this would be about 40 per cent of λ_0 (50) or about 20. The remainder, 38, would

² The conclusion of deButts & Wall (37) that Kern's conductance data shows a molecular weight dependence appears to be the result of an error in transcribing the data.

then be the limiting ionic conductance of the polyion. A similar interpretation can be made of the conductance data on neutralized pectins (38).

Strong polyelectrolytes.—Aside from scattered observations on naturally occurring strong polyelectrolytes such as agar-agar, the first systematic work with these substances was likewise carried out by Kern (30), who found that Λ for polytrimethylenedimethylammonium bromide in water increased, first gradually and then sharply, upon dilution, eventually reaching values almost equal to λ_0 for Br^- . More recently Fuoss and his collaborators have measured Λ of poly-4-vinylpyridinium chloride and bromide (31) and the polyester obtained from methyldiethanolamine and succinic anhydride (39). The concentration dependence in these cases is much like that of Kern's polyelectrolyte and of sodium polymethacrylate. The curvature persists when Λ is plotted against \sqrt{c} except at the lowest concentrations. This formal correspondence to the behavior of weak electrolytes is, however, without significance. Instead, the behavior appears to reflect the increasing conductance of the polyion superimposed on the normal contribution of the unassociated counter ions. However, the conductance of the polyion must depend upon the extent of ion association, its concentration dependence, if any, and the lowering of the mobility of the polyion because of its expansion upon dilution (see below), all of which can vary from system to system. Thus qualitative differences are expected and are found; the quantitative resolution of these contributing factors remains to be accomplished.

By preparing *n*-butyl bromide addition compounds with 4-vinylpyridine styrene copolymers Cathers & Fuoss (40) were able to measure conductance as a function of the dielectric constant in nitromethane-dioxane mixtures and as a function of the number of charged groups. This produced further evidence of ion association. In particular, $\log \Lambda$ was found to decrease linearly with reciprocal dielectric constant as had also been found in water-ethanol solutions of poly-4-vinylpyridinium bromide (31). Moreover, it was also shown that Λ decreased with increasing density of charged groups (vinyl pyridine) in the chain, indicating increased ion binding.

There is considerable evidence that ionic mobilities are not significantly altered by changes in macroscopic viscosity resulting from polymer molecules (4, 38, 41). However, Edelson & Fuoss (42) showed that the conductance of NaBr in polyvinyl alcohol solutions, in which the polyvinyl alcohol concentration was the same but its degree of polymerization varied, decreases with increasing degree of polymerization. If this conclusion proves to be generally valid, some estimates of the specific conductivity of the counter ion in polyelectrolytes will have to be reconsidered.

TRANSFERENCE

The measurement of transference numbers, and hence the extent of ionic association, is due largely to Wall and his collaborators. Their first measurements were with PAA using the classical Hittorf method (43). The transference number of the polyion, t^- , was found to have a small but readily measurable value of 0.01 at 3 per cent and to increase upon dilution toward

a limiting value of 0.04; this increase was directly proportional to the increasing charge on the polyion as a result of ionization. Thus the transport of current by the polyion is finite but quite small. It is within the probable error of Kern's experiments which indicated a zero value for t^- .

With neutralized polyacrylic acid and other strong polyelectrolytes, ionic association prevents the direct use of this method, since not only the net transport of polyions but also their effective charge is required. An elegant modification of the Hittorf method, employing radioactive sodium to measure the net transport of Na^+ , has been developed by Wall and co-workers (41). In this way the fraction of Na^+ associated has been found to be about equal to α up to a value of 0.4 and then to increase less rapidly reaching a value of about 0.65 at complete neutralization. Thus the polyion conducts nearly half the current in the range of 25 to 100 per cent neutralization. Indeed, in the vicinity of complete neutralization the net transport of Na^+ is toward the cathode because the major part of it is associated. Alternatively, the results can be expressed in terms of the equivalent ionic conductance of the polyion: at 0.0151 *N*, λ_p increases from 30 at $\alpha=0.1$ and passes through a flat maximum of 50 at $\alpha=0.6$. These results confirm the earlier estimates of Kern which he himself ignored at times. The fact that λ_p passes through a maximum, whereas the net charge increases monotonically, albeit slowly, with α is very probably the result of the expansion of the polyion; the increased frictional resistance more than compensates for the increase in net charge.

Somewhat similar information has been obtained on polyvinylpyridinium iodide (44); the value of t^- falls linearly from 0.23 with increasing α and the fraction of I^- associated is considerably less than the Na^+ associated with polyacrylate ions.

The measurement of the diffusion of Na^+ in a solution of a sodium polysalt offers another method of determining the fraction of Na^+ associated with the polyions, since only that fraction which is unassociated is free to diffuse. Huizenga, Grieger & Wall (45) have measured the steady state diffusion in this manner in sodium polymethacrylate solution and obtained results in very close agreement with those of transference experiments.

ELECTROPHORESIS

Although there are a number of electrophoretic measurements on polyelectrolytes, only two investigations are concerned with the general aspects of polyelectrolyte behavior as well as the characterization of a particular substance. One of these is the study of pectin by Saverborn (38), whose conductivity measurements were discussed above. He showed that the electrophoretic mobility increased with charge (pH), was only slightly dependent on concentration down to 0.1 per cent, but increased with decreasing ionic strength, the effect being pronounced below 0.1 ionic strength. The value of the mobility rose from 15.9×10^{-6} cm.² sec. volt⁻¹ at 0.1 ionic strength and pH 7.0 to 44×10^{-6} at 0.001 ionic strength at pH 5.8. This increase in mobility to values comparable with that of small ions (Na^+ is 47×10^{-6}) is at-

tained, apparently, despite a pronounced swelling of the molecule, which would in itself suppress the mobility, and must therefore be assigned to the decreased effectiveness in shielding of the polyion charge by the expanded counterion atmosphere. The mobility of aqueous solutions (unneutralized) was found to be about 10×10^{-5} . This together with the conductivity measurements permitted an estimate of 0.03 to 0.05 for the transference number. This estimate compares favorably with the values of Wall on PAA, keeping in mind that pectin is a stronger acid. Similar results were observed for gum arabic solutions where, in addition, it was found that multivalent cations (counterions) even at concentrations of 0.005 *N* lowered the mobility several-fold and, conversely, multivalent anions enhanced it by a similar amount.

The other electrophoretic study in which both ionic strength and pH were varied is that of Creeth, Jordan & Gulland (46) on desoxypentose nucleic acid, a polyampholyte. They likewise found a pronounced increase of mobility with concentration although the viscosity varied tenfold. The pH dependence of the mobility bore a marked relation to the titration curves and was the subject of an attempt to relate mobility to net charge (47). Although the result indicated considerable ionic association, the validity of such a calculation becomes more in doubt as the theory of electrophoretic mobility is investigated (8, 9).

The mobility of desoxypentose nucleic acids under more limited sets of conditions has been the object of a number of recent investigations (48, 49, 50). Electrophoresis has been used to study the relative heterogeneity of pectin samples (51). The variation of mobility with pH for two synthetic polyampholytes has been reported (52, 53); in these cases the mobility passed through zero at the isoelectric point as expected.

SEDIMENTATION AND DIFFUSION

At sufficiently high ionic strength counterion atmospheres will be sufficiently collapsed so that each charge on the polyelectrolyte will be individually shielded. As a result its macromolecular behavior (see the next two sections) will be quite like that of an uncharged polymer. In agreement with this conclusion, Lamm's (54) detailed theory shows that charge effects become negligible in dilute polyelectrolyte solutions at roughly 0.1 ionic strength. The measurement of sedimentation constants, *s*, and diffusion constants, *D*, for pectin in 0.2 *N* NaCl give every indication of normal behavior uncomplicated by charge effects (38), and therefore permit an accurate determination of molecular weight using Svedberg's equation. The same normal and reproducible behavior of *s* is found with desoxypentose nucleic acid (55). In the sedimentation of pectin, it was shown that the value of *s* was independent of the nature of the monovalent counterion, but that it increased about 15 per cent in the presence of divalent and trivalent counterions, presumably as the result of ionic binding.

The value of *s* will be expected to fall with decreasing ionic strength as a result of: (a) the potential set up between the sedimenting polyion and the counterions which are hardly affected by the centrifugal field, and (b) the

expansion of the polyion discussed in the next section. On the other hand, the value of D will be expected to increase with decreasing ionic strength, because the counterions by diffusing ahead of the polyions will create a self-potential which will accelerate the diffusion of the polyions; this effect should overshadow the increase of the frictional constant which comes from polyion expansion. These expectations are most clearly shown in the work of Saverborn on pectin (38).³ The value of s decreases from 1.6 to 0.8 upon passing from an ionic strength of 0.1 to 0.001. Over the same range the value of D increased from 2.0 to 6.0 and in pure water reached 40. There is no adequate theory for these effects and until there is, it appears that such studies can lead to qualitative information about the separation of counterions and polyions but tell little about the size or interaction of the polyelectrolyte molecules.

VISCOSITY

The electrochemical behavior of polyelectrolytes, as outlined in the foregoing sections, reflects in many ways the consequences of the high concentration of electric charge, potential or real, that is characteristic of this type of macromolecule. In this behavior, however, there has been no clear indication of what effect this high electric field exerts on the flexible chain molecules. It now seems rather evident that with increasing charge density and decreasing ionic strength the coiled polymer would expand. Such an effect should be readily displayed in the physical properties of such solutions, particularly in their viscosity. Indeed this is the case, as can be seen in measurements of more than twenty years ago. However, it was not until 1948 that it was properly interpreted.

Aqueous solutions of polysalts.—The viscosity of a nonelectrolyte polymer solution is generally found to be represented by a straight line of positive slope when the reduced viscosity, η_{sp}/c , is plotted against c . Polyelectrolytes in solutions of moderate ionic strength behave similarly. However, in the absence of added electrolyte η_{sp}/c rises upon dilution in a striking manner. This behavior is shown in Figure 1a for the sodium salt of desoxypentose nucleic acid (56), this being typical of some of the earliest measurements and in Figure 1b for polyvinylbutylpyridinium bromide (the uppermost curve with open circles) (57). Similar observations have been made on sodium polyacrylate (58) agar (59), the sodium salts of desoxyribonucleic acid (60), pectinic acid (38, 61), hyaluronic acid (62), *Pneumococcus* polysaccharide, Type III (63), polystyrene sulfonate (64), polymethacrylic acid (21) in aqueous solutions, and poly- ϵ -caproamides in formic acid (65). The earlier attempts to explain this behavior as the result of disaggregation or increased hydration upon dilution are easily ruled out. The suggestion that this is a display of the classical electroviscous effect (66), that is, the increase in viscosity owing to the counterion atmosphere surrounding the macromolecule, is a more serious one but it does not appear to stand up well when one considers

³ Similar results have been obtained for polyvinylpyridinium bromide by Eirich and co-workers (83).

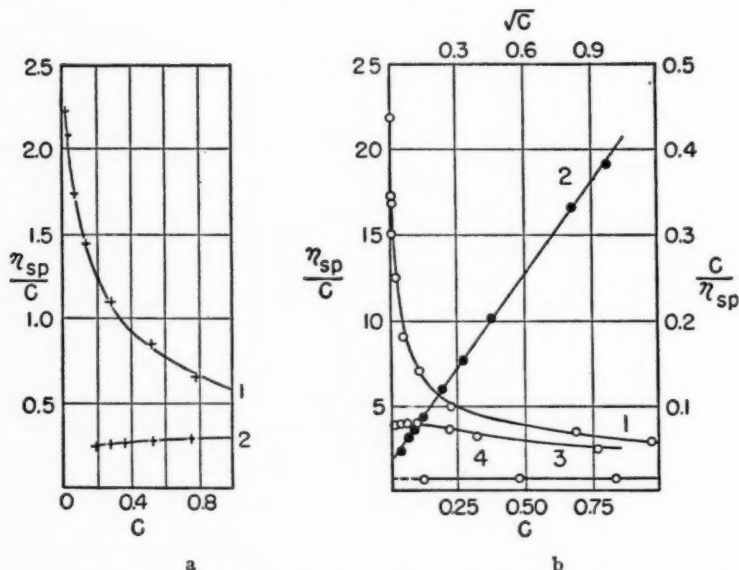


FIG. 1. (a) Reduced viscosity of sodium thymus nucleate solutions. C = concentration relative to that of the most concentrated solution investigated. Curve 1, $C_{\max} = 0.164$ per cent, solvent-water. Curve 2, $C_{\max} = 0.211$ per cent, solvent-0.005 N KCl (56). (b) Reduced viscosity of polyvinylbutylpyridinium bromide solutions. Curve 1, solvent-water. Curve 3, solvent-0.001 N KBr. Curve 4, solvent-0.0335 N KBr. Co-ordinates for 1, 3, 4 left and below. Curve 4, solvent-water, co-ordinates right and above (57).

the physical picture (67). To explain typical results in this manner one would have to imagine that several hundred counterions in a spherical volume of about a 1000 \AA diameter could act as an impermeable sphere. Actually the electroviscous effect in suspensions of rigid charged particles has been found to be relatively small (68, 69). In 1948 it was independently proposed by Fuoss & Strauss (70), Hermans & Overbeek (71), and Kuhn, Kunzle & Katchalsky (72) that the increase of the reduced viscosity upon dilution was due to the expansion of the coiled polyion. The latter two groups of investigators were particularly concerned with the theory of this effect, upon which comment is made in the final section.

Fuoss & Strauss (73) showed that the highly curved reduced viscosity plot could be transformed to a linear one by plotting c/η_{sp} against $c^{1/2}$ as shown in Figure 1b. Thus for a polysalt

$$\frac{\eta_{sp}}{c} = \frac{A}{1 + B\sqrt{c}} \quad 18.$$

This implies that η_{sp}/c has a finite intercept, A , at zero concentration which

one might interpret as the intrinsic viscosity of the polyion in its most swollen state. The interpretation of data on partially neutralized PMA in this way, using the Flory-Fox equation (74), leads to the conclusion that the maximum size of the polyion was in this case about 40 per cent of its contour length (21). Light-scattering measurements mentioned below checked this conclusion. The apparent existence of a finite intercept for polyelectrolytes contrasts with the absence of one in ordinary electrolytes. In the latter case the viscosity is due to the distortion of the counterion cloud, and this, as well as the viscosity it gives rise to, goes to infinity, in principle, upon dilution. The polyion, instead, appears to expand along with its counterions but approaches a definite limiting size. The indication that this size is smaller than the completely extended polyion implies that even at this extrapolated limit many of the counterions remain with the polyion (21).

The pH dependence of the viscosity of polyampholytes in the absence of added electrolyte is characteristic as has been known for a long time in the case of gelatin. The viscosity is, of course, relatively low at the isoelectric point, but upon increasing or decreasing the pH the viscosity rises in consequence of the uncoiling and in the limit of extremes of pH falls again because of the building up of an excess of counterions. Such behavior in synthetic polyampholytes is particularly pronounced and has been studied in detail (33, 34, 35).

Effect of ionic strength and dielectric constant.—As the ionic strength of the solvent is increased, the reduced viscosity plots fall toward the linear type characteristic of a swamping excess of electrolyte in an interesting fashion that has been explored for polyvinylbutylpyridinium bromide, one curve of which has been included in Figure 1b (58), sodium pectinate (61), and sodium polyacrylate (67). Upon passing through a family of curves corresponding to increasing ionic strength, a sharp maximum is found to develop at quite low concentrations and to move outward and to flatten with increasing ionic strength, finally disappearing as the plot becomes linear. This maximum appears to correspond to a transition between two regions, in one of which the counterion concentration derives principally from the polysalt (high polymer concentration) and in the other of which the counterions are principally those which are the result of the constant ionic strength of the solvent (low polymer concentration). In this latter region, where the counterion concentration is relatively constant, a normal linear plot is expected and is observed.

Upon going to very high ionic strength, it is found (57) that the reduced viscosity, and hence the intrinsic viscosity, fall considerably below the values expected for the same polymer when it is discharged by chemical reaction with the iogenic groups. This result, if shown to be generally true, indicates that there is a supercontraction of the polymer coil, probably like that which occurs with nonelectrolyte polymers in poor solvents, which may indeed be a prelude to salting out at still higher ionic strengths.

The alternative way to study the effect of added electrolyte is to maintain the concentration of the polymer constant and alter the concentration and type of added electrolyte. In some of the earliest experiments it was

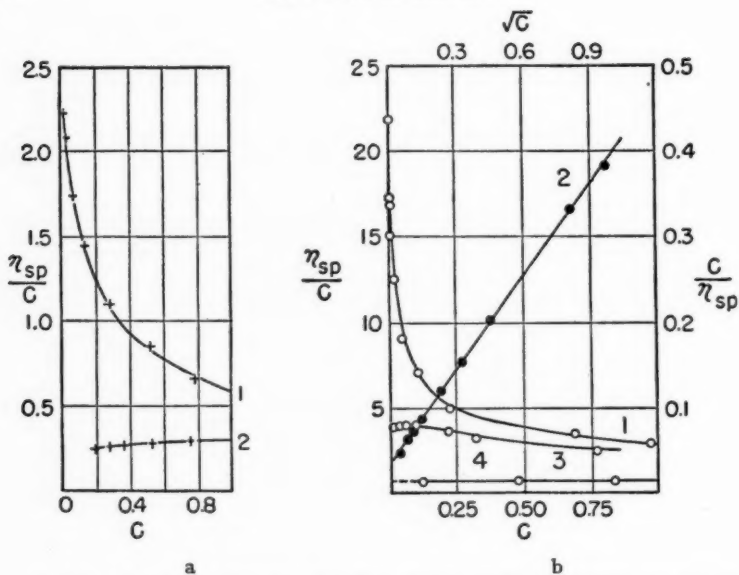


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The alternative way to study the effect of added electrolyte is to maintain the concentration of the polymer constant and alter the concentration and type of added electrolyte. In some of the earliest experiments it was

noted that the decrease in viscosity depended only on the valence of the counterion (75). This behavior has been confirmed and studied in detail in PAA by Markovitz & Kimball (67). The much greater effect of divalent, in contrast to monovalent, counterions is quite striking.

Although the term $B\sqrt{c}$ appearing in equation 18 appears to be electrostatic in origin, no theoretical interpretation has been given, nor has any been given for the corresponding term in the equation representing the viscosity of ordinary electrolytes. Empirically, it has been found that the coefficient B varies inversely as the square of the dielectric constant (76) and that it increases with the effective charge on the polyion; it is only slightly dependent on molecular weight (21).⁴

Reduced viscosity at constant counterion concentration.—Having seen that the viscosity and hence, probably, the size of the polyion is so sensitive to the concentration of counterions, it follows that by maintaining the concentration of counterions constant as the polyion concentration is varied, one may expect to stabilize the size of the polyion and hence obtain a linear plot of η_{sp}/c against c , which would permit a determination of the intrinsic viscosity and therefore an estimate of polyion size as a function of counterion concentration. There is evidence from light scattering that such a procedure does stabilize the size of the counterion atmosphere about a charged protein molecule (77). Pals & Hermans (61) have shown that linear plots are obtained when sodium pectinate solutions are diluted with NaCl solutions in which the equivalent concentration of the Na^+ is 1.5 times that of the sodium pectinate solution.⁵ The curvature that would have resulted had the Na^+ concentrations been equal may indeed have been only that expected in solutions in which the interaction is so great. In any event this approach shows considerable promise. In particular it may lead to an estimate of the relative contribution to η_{sp}/c of the size of the polyions and their interactions. Certainly until it is proven otherwise, one must assume that both contribute considerably and that the size of the polyion at finite concentration cannot be estimated from the value of η_{sp}/c as has sometimes been done (72).

Intrinsic viscosity-molecular weight relations.—The coefficient a in the well known relation between intrinsic viscosity and molecular weight of polymers:

$$[\eta] = KM^a \quad 19.$$

has a value of 0.5 for a relatively tight coil ("solvent immobilizing" or "devoid of long-range interactions"), of 1.0 for a more open but still random coil ("free draining") and of 2.0 for rigid rods in the limit of low molecular weights (78, 79). Therefore, with the proper extrapolation of viscosity data

⁴ The influence of the dielectric constant of the medium upon the viscosity of polyelectrolytes has recently been explored for solutions of cellulose xanthate [Tait *et al.* (118)] and carboxymethylcellulose [Basu & Das Gupta (119)], for both of which an increase in viscosity with dielectric constant was observed.

⁵ For carboxymethylcellulose (61), however, it was found that an equivalent concentration of NaCl sufficed to prevent curvature. Similar results have also been recently obtained for polyvinylpyridinium bromide (83).

and independent molecular weight measurements, the determination of a should lead to an estimate of the extent of expansion of the polyion. The first attempt at this for sodium polymethacrylate in aqueous solution led to a value of $a = 2$ (80) but must be accepted as a qualitative estimate inasmuch as η_{sp}/c at finite concentrations was used. In two other applications of this method extrapolation according to equation 19 was employed, but there was insufficient data to lead to a precise result. One of these cases concerned nylon in formic acid, $a = 2$ (57) and the other was sodium polymethacrylate, $a = 1.87$ (21). These results show the polyion at infinite dilution to be highly expanded but are not of sufficient precision to lead to quantitative conclusions.

In moderate ionic strength solvents polyions are expected to behave as nonelectrolyte polymers in regard to their size and therefore the value of a should be in the normal range of 0.6 to 0.8. The only direct evidence thus far is that sodium polymethacrylate in 2*N* NaNO₃ (19) and in 2*N* NaOH (21) exhibited a value of a close to 0.76, the value for the methyl ester of polyacid in benzene. There is consequently little doubt that with proper precautions useful intrinsic viscosity-molecular weight relations can be established for polyelectrolytes in solutions of moderate ionic strength.

STREAMING BIREFRINGENCE

Both extinction angle and magnitude of birefringence as determined in streaming birefringence experiments are sensitive expressions of the molecular asymmetry of the solute molecules. The expansion of polyions upon dilution of their aqueous solutions should therefore be readily demonstrable by such measurements. An investigation of sodium desoxypentose nucleate over a range of ionic strengths from 10^{-4} to 1 failed to reveal any significant change in extinction angle with ionic strength (81). This was interpreted by the authors as evidence for a rigid structure for the molecule. The anticipated effect was clearly evident in the experiments of Kuhn and co-workers (72) on polymethacrylic acid. The limiting slope of extinction angle versus gradient at zero gradient was found to rise rapidly from a very low value at zero degree of neutralization, leveling off at degree of neutralization equal to 0.5; the curve follows very closely the curve of η_{sp}/c in the same system.

In the experiments of Fuoss & Signer (82), the changes of extinction angle and amount of birefringence were studied on diluting salt-free solutions of the strong polyelectrolyte polyvinylbutylpyridinium bromide. Extinction angles were found to vary but little on dilution, while intensity of birefringence went through a maximum as a function of concentration. The first observation may be regarded as resulting from two opposing effects: extension of the molecule on dilution tending to lower the value of the extinction angle, and the reduced interaction between neighboring molecules tending to raise it. The maximum in the intensity of birefringence as a function of concentration is in marked contrast to nonelectrolyte polymers which exhibit a linear or more rapid decrease of intensity on dilution. The behavior of the polysalt is clearly consistent with an increase in the anisotropy of the molecule on dilution, corresponding to a greatly extended chain.

Rosen, Kamath & Eirich (83) have found results in qualitative agreement with this picture on studies of the same polymer in which dilutions were carried out at constant counterion concentration. These authors stress the necessity of taking molecular interactions into account in interpreting measurements of this type.

EQUILIBRIUM PROPERTIES OF POLYELECTROLYTES

SOLUBILITY

The importance of the charge and concentration of counterions in determining the inter- and intra-molecular interactions of polyelectrolytes has been strikingly shown by studies of their dynamic solution properties; although thermodynamic methods have not yet been fully exploited in the characterization of polyelectrolytes, the growing body of information in this field has served to substantiate, and in some cases to expand, our concepts of the significance of electrostatic effects in determining the configuration and interaction of polyions.

Little quantitative information is so far available on the degree to which such interactions are reflected in the solubility properties of adequately characterized polyelectrolytes. Studies on synthetic polyacids (PAA, PMA) as well as on pectic acids subjected to controlled esterification by newly perfected techniques (84, 85) indicate that the formation of gels upon addition of divalent ions is the result of specific interaction rather than of a general salting out effect. Thus 0.002 *N* barium chloride precipitates completely deesterified sodium pectinate in 0.0078 *N* solution (86); approximately 0.0013 *N* barium hydroxide will bring about the gelation of 0.009 *N* PAA (87). These experiments indicate, moreover, that the ionized carboxyl groups are involved in the reaction leading to precipitation. In general, the effectiveness of divalent ions in causing gelation of these polyacids increases with the ionic radius; however, Kern (88) observed that PAA did not precipitate with tetramethylethylenediamine. The solubility of the polyacids appears very sensitive to the detailed structure of the polyion, as indicated by the different solubility behavior of PAA and PMA (89) and by the importance of the method and extent of de-esterification in determining the interactions of ions with pectin (90, 91).

The mutual precipitation of polyions of opposite charges has been reported by Staudinger & von Becker (92), who observed the formation of a salt on mixing equivalent amounts of sodium polyacrylate and polytrimethylenedimethylammonium bromide. Fuoss & Sadek (93) reported similar results for poly-4-vinyl-*N*-*n*-butylpyridinium bromide with both sodium polyacrylate and sodium polystyrene-sulphonate, and Morawetz & Hughes (94) have recently studied the interaction of polyacids, -bases, and -ampholytes with bovine serum albumin, in the hope of utilizing synthetic materials for the fractionation of proteins. Polyampholytes themselves present a particularly interesting problem, since in one and the same linear molecule oppositely charged groups are available for interaction. The cause of the insolubility of copolymers of acrylic or methacrylic acid and 2-vinyl-

pyridine (32, 33) at the isoelectric point cannot be assessed at present, because of the conflicting evidence about the state of ionization of the carboxyl and pyridine groups (34). However, it appears from the work of Doty & Ehrlich (36) and Alfrey *et al.* (35) on water soluble copolymers of methacrylic acid with 2-dialkylaminoethyl methacrylate that electrostatic interaction of positive and negative groups is significant, resulting in partial aggregation at the isoelectric point. To achieve a clearer picture of the effects of multivalent counterions on the interactions between polyelectrolyte segments, quantitative investigations of the changes in configuration, as is for instance possible by light-scattering measurements, as well as of the binding of such counterions, are indicated.

SURFACE CHEMISTRY

Investigations of monolayers of polyelectrolytes have been extremely limited both in number and in scope because of the difficulties of obtaining stable films on pure water; although salt or acid substrates do make such experiments possible, the large concentration of counterions present swamps the electrostatic interactions which are of particular interest. Crisp (95) studied PAA and PMA films at low pH's, solution occurring if the polyacid was ionized. The surface moment of these films was only of the order of 30–40 millidebye, probably as a result of extensive hydrogen-bonding between carboxyl groups. This same hypothesis was advanced by Cumper & Alexander (96) to explain measurements of the surface viscosity of PMA at a petroleum ether-water interface. It is interesting to note that hydrogen bonding can play an important part in determining the configuration of polyacid chains in solution, resulting, according to Katchalsky (80), in a rigid, hypercoiled structure.

Allan & Alexander (97) have investigated monolayers of strong polyelectrolytes, obtained by quaternizing copolymers of 4-vinylpyridine and styrene. They conclude that at an air-water interface the counterion-pyridinium ion system forms a two dimensional lattice, resulting in a negative contribution to the enthalpy of spreading. The experimental value for this enthalpy term is not in good agreement with that calculated for a simple two dimensional lattice, however.

Measurements on adsorbed films of PMA at the air-water interface have recently been carried out by Katchalsky & Miller (98), and here again the high density of ionizable groups results in anomalous behavior. Upon ionization, it was observed that the surface pressure of PMA fell much more rapidly than that of isobutyric acid, and the monomeric analogue. The investigators attribute the different behavior to the fact that upon ionization of the monomeric acid, the un-ionized species are preferentially adsorbed; for the polyacid, such a separation into charged and uncharged species does not occur, and the surface activity drops sharply as the number of ionized groups along the polymer chain is increased. Addition of sodium chloride suppresses electrostatic interactions, and, as expected, brings about an increase in surface pressure.

OSMOTIC PRESSURE

Kern, whose extensive investigations of the titration and transport properties of polyacids formed the basis of much of the later work in these fields, also pioneered in the application of thermodynamic measurements to the study of solutions of polyacrylic acid and its salts. The importance of the field of the ionized groups in determining the configuration of the macromolecules, as well as the arrangement of counterions, as reflected in the viscosity, conductivity, and titration of polyelectrolytes, has already been discussed. The results of Kern's (4) osmotic pressure measurements on highly charged PAA again emphasize the particularly strong forces operative between the polyions and the surrounding counterions. Since the osmotic pressure is responsive to the number of particles in solution, and not to their size, the influence of the counterions predominates in the two component system water-polyelectrolyte (99). For polyacrylic acid (PAA) in dilute aqueous solution ($c_A=0.0625\text{ }N$) Kern found that the osmotic coefficients were of the order 0.8.⁶ On neutralization with sodium hydroxide, however, the coefficients fell gradually, reaching a value of 0.2 at 80 per cent neutralization (4);⁷ at any given extent of neutralization, the osmotic coefficients changed only slightly with concentration, decreasing with increasing dilution. This inactivation of the counterions was also shown by measurements of the activity of Na^+ in neutralized PAA, using a sodium amalgam electrode (101). Cryoscopic measurements on partly neutralized PAA corroborate these results (4). In contrast, 0.1 N isobutyric acid, at the same degree of neutralization, gave activity coefficients of approximately 0.9, which, upon dilution, approached unity (101). Wall's recent investigation of the binding of Na^+ by PAA (41, 45), using radioactive tracers, leads to lower values for the number of bound ions than those obtained from osmotic pressure measurements (on the assumption of the validity of van't Hoff's law), but the qualitative features of the dynamic and equilibrium measurements are in good agreement. The interaction of a charged polyion with its counterion cloud depends almost entirely on the valence of the small ion, and, as already found in titrations (4), is not sensitive to the molecular weight (4), nor to the size of the counterions. For PAA 60 per cent neutralized with lithium, sodium and potassium hydroxide, the osmotic coefficients are identical within the limit of error (88); for salts with organic bases, such as methyl and benzyl amine, the variation in the osmotic coefficient still is only 10 per cent. An increase in the charge of the counterions, however, results in greatly marked differences. Because of the insolubility of the alkaline-earth salts of PAA, Kern (88) investigated tetramethylethylenediamine salts, for which the osmotic coefficient was less than 3/4 that of alkali salts. Similar observations on the effects of divalent ions on polyacids were already made by Oakley (102), who calculated the extent of association of Na^+ and Ca^{++} salts of gum

⁶ Kern's neglect of the contribution of the macroion to the osmotic pressure is not justified for low molecular weight samples, $P < 900$.

⁷ Briggs' (100) studies on the osmotic pressure of the sodium salt of gum arabic show a similar dependence of the osmotic coefficient on the degree of neutralization.

arabic from their osmotic pressure and found that it increased from 70 per cent to 82 per cent for the divalent counterion.

There is so far little evidence on the dependence of these interactions on the structure of the polyion itself. Kern & Brenneisen (30) performed osmotic pressure measurements on polytrimethylenedimethylammonium bromide, $[\text{Br}^-\text{N}^+(\text{CH}_3)_2-\text{CH}_2-\text{CH}_2-\text{CH}_2]_x$ aqueous solutions of which gave osmotic coefficients of approximately the same magnitude as sodium polyacrylate. For polydecamethylenetetramethylethylenediammonium bromide, $[(\text{CH}_2)_{10}\text{Br}^-\text{N}^+(\text{CH}_3)_2-\text{CH}_2-\text{CH}_2-\text{N}^+\text{Br}(\text{CH}_3)_2]_x$ in which pairs of positive centers are separated by 10 methylene groups and the average separation of charges is therefore greater than in the above polymer, there occurred very considerable exchange of Br^- for OH^- in the osmometer, and the osmotic coefficients were considerably higher. Although this membrane hydrolysis prevented a quantitative evaluation of the coefficients, the fact that bromide ion exchange was pronounced, itself points to considerably smaller interactions. Measurements on alkali salts of pectic acid, performed in Kern's laboratory (30), indicated a similar dependence of interaction on the separation of charged groups, but detailed results have not been published. However, these observations are corroborated by Fuoss' conductivity measurements on quaternized copolymers of vinylpyridine and styrene (40) which revealed that the binding of bromide ions increased with the number of charged groups on the polymer.

The interactions between polyion and its surrounding counterion cloud should clearly be dependent upon the nature of the solvent, and this is demonstrated by the results of the osmotic pressure measurements of Strauss & Fuoss (103) on poly-4-vinyl-N-*n*-butylpyridinium bromide. In ethanol, the osmotic pressure was only one-twentieth of that calculated for the bromide ions, indicating that association is increased as the dielectric constant of the medium is lowered. Experimental difficulties make an interpretation of the results at low concentrations uncertain, but it appears that the reduced osmotic pressure increased with increasing dilution, indicating a decrease in the number of bound bromide ions upon dilution. Moreover, the osmotic pressure of this polyelectrolyte in pure ethanol was found to depend on the molecular weight, a polymer of degree of polymerization 730 giving pressures approximately 30 per cent higher than one of degree of polymerization 2000. These conclusions are in conflict with the work of Wall (41, 45) and Kern (4, 101) on the dependence of binding on concentration of sodium polyacrylate, as well as with Kern's (4) osmotic pressure measurements, which, in aqueous solution, did not show a dependence on molecular weight. Since the work of Strauss & Fuoss is, in all essentials, in disagreement with experiments on aqueous polysalt solutions, a re-examination of their anomalous results is indicated.

So far, osmotic pressure measurements have not been used to any extent for the determination of molecular weights, although, just as in the case of proteins, the reduced osmotic pressure at infinite dilution in the presence of a third component, such as salt or acid, is equal to the reciprocal of the

molecular weight times RT . Dobry & Boyer-Kawenoki (104) have used this technique to obtain the molecular weight of PAA from measurements in 1.2 N HCl.⁸ Strauss & Fuoss (103), who measured the osmotic pressure of poly-4-vinyl- N - n -butylpyridinium bromide in ethanol in the presence of 0.61 N LiBr, claim to have obtained a limiting reduced pressure 1.45 times that expected from the known molecular weight. This is contrary to the result predicted by thermodynamics (105), and must be treated with reservation.

LIGHT SCATTERING

In contrast to the osmotic pressure, which, for polyelectrolytes in aqueous solution depends on the counterions and their interactions with the polyions, light-scattering measurements are indicative of the size and form of the polyions and their mutual arrangement in solution. The application of this technique to the study of inter- and intramolecular interactions of polyelectrolytes is a natural extension of the work already done on proteins, which has been recently reviewed by Doty & Edsall (106). For PMA in aqueous solution, Oth & Doty (21) observed that upon increasing the extent of neutralization, the effective diameter of the spheres of action, by which the distribution of the polyions may be characterized, increased, this increase being reflected in an increase in the initial slope of Kc/R_{90} against concentration. However, from 25 to 71 per cent neutralization, the data for a fraction of degree of polymerization 1000 showed only a very small response to changes in the charge on the polymer coil, and was of the same order of magnitude as that for serum albumin with only 50 charges. Two factors appear to be responsible for this behavior—the binding of counterions with increasing degree of neutralization, which keeps the effective charge fraction, that is, the ratio of net charge to total number of carboxyl groups, between 0.20 and 0.35 over this range of neutralization (21), and the flexibility of the polymer chain, which permits a distension of the coil upon increasing the net charge. Both of these serve to keep the charge density, and thus the effective diameter of the coil at a given polyion concentration nearly constant.

Since the dissymmetry of the scattering envelope at infinite dilution is a function of the size of the polyion, Oth & Doty were able to follow the expansion of PMA upon addition of NaOH. From 0 to 25 per cent neutralization, the root mean square separation of the ends of the polymer coil (R_z) increased from 210 Å to 940 Å; at a degree of neutralization of 0.7, R_z only achieved a value of 1180 Å. however, because of the increase in the number of bound Na^+ . These findings substantiate the picture of a loose molecular coil, with dimensions responsive to the net charge, which was put forth by Fuoss & Strauss (70), Hermans & Overbeek (71), and Kuhn, Kunzle, &

⁸ Note added in proof: Pals & Hermans (61) have obtained the molecular weight of sodium pectinate and carboxymethylcellulose at various concentrations of added salt. As expected from the Donnan condition, the slopes of the reduced osmotic pressure curves against concentration increase with decreasing salt concentration; the molecular weights are, however, unchanged.

Katchalsky (72) to explain the anomalous viscosities observed for polyelectrolyte solutions.

For charged PMA, the dissymmetry as a function of concentration showed a broad minimum similar to that already observed for bovine serum albumin by Doty & Steiner (77). Although the decrease in the dissymmetry with increasing concentration can be ascribed to an ordering in solution brought about by the long range electrostatic forces operative between polyions in solution, a satisfactory explanation of this phenomenon for polyions has so far not been presented for bovine serum albumin; however, Doty & Steiner (77) have been able to give a quantitative discussion of the factors responsible for this concentration dependence. Fuoss & Edelson (107) have investigated the light scattering of solutions of poly-4-vinyl-*N-n*-butylpyridinium bromide, and observed a similar dependence of the dissymmetry on the concentration. Addition of salt reduced this minimum, and 1 *N* KBr eliminated all concentration dependence, as electrostatic interactions were suppressed.

Wall and co-workers (108), as well as Katchalsky & Eisenberg (80), and Dobry & Boyer-Kawenoki (104) have measured scattering from PAA and PMA in the presence of buffers or HCl, and have been able to obtain an estimate of the molecular weight. This procedure, while quite proper for molecular weight determinations, obscures the detailed changes in the structure and arrangement of polyelectrolyte molecules which occur with concentration and charge.

The techniques of light scattering have recently been applied to the study of synthetic polyampholytes by Wagner & Long (32) and Doty & Ehrlich (36). The latter, who studied a copolymer of methacrylic acid and 2-dimethylaminoethyl methacrylate, soluble over the whole pH range, found that at the isoionic point, the polyampholyte tended to associate, as indicated by a negative second virial coefficient. In 0.1 *N* NaCl, this aggregation was suppressed, however, and the behavior of the polyampholyte was that to be expected for an ordinary polymer in a good solvent, such as, for example, polystyrene in toluene. Measurements of the viscosity, both in the presence and in the absence of salt (36, 33), corroborate this interpretation of the light-scattering experiments. The mutual compensation of oppositely charged polymer segments, without the intrusion of foreign counterions, thus represents a unique example of the very strong interaction resulting from the field set up by the charge centers on ionized polyelectrolyte molecules, which is responsible for the characteristic behavior of polyelectrolyte systems as deduced from measurements of their dynamic and equilibrium solution properties.

Only recently, the submicroscopic changes in the configuration of polyelectrolytes, which are so clearly indicated in the light-scattering experiments, have been visualized on a macroscopic scale by several investigators (109 to 113) through the expedient of the cross-linking of polyacid chains into three-dimensional networks. The filaments thus obtained are capable of supporting weights, and expand or contract with changes in the hydrogen

ion concentration of the surrounding medium. These polyelectrolyte threads, which in their general behavior resemble muscles, thus provide a system which permits the reversible conversion of chemical into mechanical energy in isothermal cycles.

THEORETICAL INVESTIGATIONS OF THE ELECTRIC FIELD ENERGY

Since 1948 there have been several ambitious attempts to construct a quantitative theory of polyelectrolyte behavior. The aim in each of these attempts has been the calculation of the electrostatic contribution to the free energy of the polyelectrolyte, F_e , since a knowledge of these permits the calculation of: (a) the change of molecular configuration upon charging and therefore also of the viscosity and light-scattering properties of polyelectrolytes, (b) the titration curves of weak polyelectrolytes, which depend on the increase of F_e with charge, and (c) the counterion distribution. Although considerable progress has been made, the present state of the theory, as well as the limitations of space, preclude any but the briefest outline of the initial developments in this field.

Kuhn, Künzle & Katchalsky (72) have calculated the electrostatic energy for a random coil with uniformly spaced charges, neglecting entirely the contribution of the counterions to the potential; Künzle (114) has generalized this treatment to include the effects of the counterions employing the Debye-Hückel approximation. Using Künzle's approach, Katchalsky has found that for solutions of medium ionic strength ($\kappa = 10^5 - 10^7$), the expression for the electrical free energy reduces to the relation (112, 113)

$$F_e = \frac{h^2 e^2}{DR} \ln \left(1 + \frac{6R}{\kappa R_0^2} \right) \quad 20.$$

where R_0 and R refer to the root mean square separation of polymer ends unperturbed by electrostatic interactions and under the influence of a net charge of h per molecule. The other symbols e , D , and κ , refer to charge of the electron, dielectric constant, and Debye's reciprocal length, respectively.

A different approach to this problem was taken by Hermans & Overbeek (71); these investigators calculated the free energy by approximating the polyelectrolyte by a sphere, with either a uniform or a Gaussian distribution of charge. The results in both of these cases can be approximately represented by

$$F_e = \frac{3}{5} \frac{h^2 e^2}{DR'} (1 + 0.6\kappa R' + 0.4\kappa^2 R'^2)^{-1} \quad 21.$$

$$R'^2 = \frac{5}{36} R_0^2 \left(1 + \frac{R^2}{R_0^2} \right). \quad 22.$$

With polyelectrolytes of high charge at low ionic strength, the potential will be much too large for the use of the Debye-Hückel approximation which is involved in the two expressions for F_e given above. An alternative approach has been outlined by Kimball, Cutler & Samelson (117), who use the Donnan

approximation to solve the Poisson-Boltzmann equation in the limit of high potential. Other difficulties, however, prevent the direct application of the results to solutions of low electrolyte content.

The necessity of finding an expression for F_e that adequately takes into account the role of the counterions, and added electrolyte as well, is emphasized by recent theoretical investigations of the distribution of counterions around rod-shaped macroions. This problem has been solved without the customary approximations by Alfrey and co-workers (115) for an array of parallel rods and by Fuoss, Katchalsky & Lifson (116) for a single rod. The results in both cases clearly indicated that a considerable fraction of counterions remained close to the charged macro-ion. It is to be expected that the same qualitative conclusion would hold for somewhat coiled polyions and consequently a theoretical formulation which solves this potential problem without the Debye-Hückel approximation remains for the future. Turning, in conclusion, to the bearing of experimental observations on these theoretical investigations, we note that the first consequence of these is the possibility of calculating the size of the polyion. The electrostatic repulsion between charged polymer segments brings about a change in the distribution of polymer segments, which is taken account of by a Boltzmann factor, giving the distribution function (72)

$$W(R)dR = \text{const.} \exp(-3R^2/2R_0^2) \exp(-F_e/kT)R^2dR. \quad 23.$$

This expression permits evaluation of the most probable end-to-end distance of a charged polymer, and therefore also of its viscosity and dissymmetry in light scattering. Arnold & Overbeek (19) have compared the viscosities for PMA in salt, calculated from the free energy expression of Hermans & Overbeek, with experimentally determined values, and found fair agreement for low degrees of ionization. Similarly, Katchalsky & Gillis (28) have evaluated pK_m and n for PMA from the theory of Kuhn, Künzle & Katchalsky, and found excellent accord with values obtained by Katchalsky & Spitnik (18). This, however, is apparently fortuitous since the parameters used in their calculations seem to have been based on improperly interpreted data (21). In the study of PMA, previously referred to (21), the values of R calculated from the titration data, using the relations given by Overbeek (29), as well as those of Kuhn *et al.* (72), are consistently higher than the values deduced from light scattering and viscosity. The discrepancies between theory and experiment are, no doubt to a large extent, brought about by the association of counterions which was completely neglected by Kuhn *et al.* (72) and treated by the Debye-Hückel approximation by others.

Recently Katchalsky and co-workers (112, 113, 120) have presented a comprehensive theory describing the titration, osmotic pressure, and equilibrium swelling of polyelectrolyte systems; a critical appraisal must, however, be postponed until detailed publication of their theoretical and experimental work.

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ION EXCHANGE¹

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A year ago Boyd (6) reviewed the rapid development of synthetic organic ion exchange resins during the period 1940 to 1950 with particular emphasis on their chemical structure, their basic physical characteristics, their exchange equilibria and rate, and their chromatographic use in analytical and preparative chemistry. This decade marked the development of ion exchange resins of clearly defined structure, monofunctionality of ionic grouping, controlled cross-linking of any desired degree, spherical particles of any diameter less than 1 mm., and uniform density of exchange groups. The development of such well-defined chemical tools has vastly simplified the interpretation of ion exchange phenomena and has stimulated the discovery of sound physical and chemical laws governing the equilibria and their rates of attainment between an ion exchange particle and its environment. This clear understanding of the true nature of ion exchange has in turn stimulated the use of exchange techniques in water treatment, chemical manufacture, waste recovery, pharmaceuticals, medical therapy, and even in the fundamental study of the nature of complex ions and their activities in solution. The art of preparing weak and strong acid cation exchangers (sulfonic and carboxylic acids) and weak and strong base anion exchangers (primary to quaternary amines) of high chemical and physical stability may well be said to have matured by the end of the decade. Future progress may be anticipated chiefly in the introduction of other functional groups or combinations of such groups to attain high selectivity for a specified ion, improved control of the concentration of the functional groups on the hydrocarbon skeleton, and in the development of stable new physical forms such as membranes, tubes, fibers, cloth, etc.

The past year has witnessed the announcement of the availability of phosphonic acid type cation exchange resins (9), the discussion of quaternary amine anion exchangers by direct vinyl-type polymerization of basic monomers (7), the presentation of the properties of exchange resins prepared by treatment of natural cotton fibers (31), the conversion of rubber to anion exchange resins by chlorination and amination (54), and additional progress on chelating resins (24).

It is well to note also the increased interest and activity during the past five years in the field of polyelectrolytes. Though this activity has grown independently of ion exchange, the two arts are fundamentally intertwined

¹ The survey of the literature pertaining to this review was concluded in February, 1952.

² The authors wish to acknowledge the efforts of H. L. Aamoth, R. A. Hobart, J. R. Skidmore, and A. C. Stringfellow in compiling the literature references.

since a polyelectrolyte is simply the linear counterpart of an exchange resin. Just as our knowledge of cross-linked nonpolar polymers stems largely from extensive work on the properties of linear polymers, a sound theory on ion exchange resins may best be developed on the basis of accurate experimental work and extensive theoretical development in the polyelectrolyte field. The missing link in all ion exchange theory has been the lack of knowledge of the ionic activities inside the resin particles, and it has been assumed that we shall always have to obtain such activities by indirect means. Polyelectrolytes offer the opportunity to measure the physico-chemical properties of the resin phase directly, since a polyelectrolyte solution separated from an electrolyte solution by a semi-permeable membrane is the equivalent of the resin-electrolyte system, as shown in Figure 1. At equilibrium the concentration of the polyelectrolyte phase will be the same as that of the resin phase, when P (the osmotic pressure developed in the polyelectrolyte case) is equal to the elastic retractive pressure of the cross-linked network of the resin. This makes possible a direct experimental determination of the osmotic pressure inside resin particles, a quantity only indirectly calculable with uncertain assumptions (23). Analyses of the polyelectrolyte phase may be accurately carried out, potentials and activities measured directly by

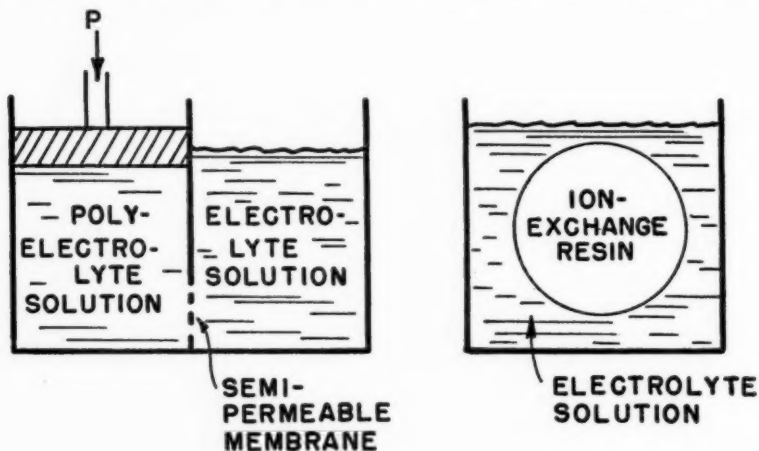


FIG. 1

inserting electrodes in the polyelectrolyte phase, and freezing points and solubilities determined in the polyelectrolyte solution. For these reasons a true understanding of ion exchange phenomena is dependent upon the development of a thorough knowledge of all the properties of polyelectrolyte solutions, particularly ionic activities at high concentrations and pressures, and it is encouraging to note the increasing number of papers in this field.

In the present review we shall attempt to cover briefly the year's ac-

accomplishments in the basic ion exchange field of exchange structure and properties discussed so thoroughly by Boyd and to add some numerical figures on such properties which may be of assistance to workers in the exchange field. We shall also attempt to cover in more detail the basic work and recent advancements in the fields of ion exchange membranes, catalysis by exchange resins, screening effects based on ionic size, methods used to characterize exchangers, and molecular adsorption in exchange resins. Much interesting work in the fields of water treatment, resin therapy in humans, analytical applications and waste recovery must be considered outside the realm of this review.

CHARACTERIZATIONS OF ION EXCHANGE RESINS

The properties of a particular exchange resin of theoretical interest include: (a) exchange capacity, (b) nature of active groups—pH dependence, (c) ion selectivity, (d) rate of exchange, (e) degree of swelling in water and electrolyte solutions of the various ionic forms, (f) density, dry and wet, (g) screening effects due to degree of cross-linking.

Other properties of particular interest from a commercial standpoint include: (a) particle size distribution, (b) pressure drop, (c) expansion on backwash, (d) solubility and color throw, (e) chemical stability, (f) physical stability-resistance to attrition, (g) temperature stability.

TYPE OF EXCHANGE GROUP AND EXCHANGE CAPACITY

Of maximum interest is the nature and concentration of the ionic groups in an exchange resin. These may be determined by direct titration of the resin suspended in an electrolyte solution of known concentration (e.g. 0.1 *N* NaCl). Standard acid or alkali is used as the titrant and a glass electrode as pH indicator. Cation exchange resins are first converted to the hydrogen form with a large excess of mineral acid; anion exchangers are similarly converted to the free base form with caustic. The resin may be dried to constant weight, preferably under vacuum, and a known weight used as basis, or, alternately, a volume of wet resin may be used as determined by settling under water in a graduate. Equilibrium pH curves for strong acid and strong base resins may be determined rapidly. Weakly acidic and basic resins will require 1 to 24 hr. to attain pH equilibrium after each incremental addition of standard acid or base. The resultant pH curve yields information both on the quantity and on the nature of all of the ionic groups in the resin.

If the capacity alone is desired, it is more rapid to add an excess of standard alkali or acid and back titrate the excess after an interval sufficient to attain equilibrium. This method is especially suitable for weakly basic resins where many of the amine groups may be extensively hydrolyzed in their salt form. A known weight or volume of the resin may also be placed in a column or a Büchner funnel and washed with an excess of NaCl solution, with subsequent titration of the filtrate for acid or alkali.

Direct chemical analysis may frequently be used where it is known that an element in the resin is present only in the ionic group: e.g., sulfur analysis

for sulfonic acid resins or nitrogen analysis for amine resins. Similarly the resin may be converted to a known ionic form (e.g., Mg^{++} or Cl^{-}), rinsed, and chemically analyzed for the ion. An ingenious method for thermochemical analysis of the total exchange capacity has recently been published (49). Conductometric titrations have also been successfully applied (63).

The approximate total exchange capacities of the principal synthetic resins are listed in Table I.

TABLE I
EXCHANGE CAPACITIES OF SYNTHETIC RESINS

Type of Structure	Dry Weight Capacity m. eq./gm.	Wet Weight Capacity m. eq./ml.
Cation Exchangers		
Sulfonated styrene-divinylbenzene	4.5-5.0	2.0-2.2
Phenolic methylene sulfonic	1.5-4.0	0.6-1.3
Carboxylic	4 -10	1 -4
Anion Exchangers		
Weak base phenolic	7 -10	1.0-2.5
Weak base styrenedivinylbenzene	5 -7	2.5-3.0
Strong base styrenedivinylbenzene	2.5-3.0	1.0-1.2

SWELLING VOLUME

The extent of swelling of an exchange resin in water and its variation with electrolyte concentration and ionic form are of practical interest in determination of required bed volume and of theoretical interest in studying ion selectivity, screening effects, and degree of cross-linking. The practical unit is simply the settled volume in water or electrolyte solution of a known dry weight of resin, and this may readily be determined by a simple measurement in a graduate or a tower. Variation in this volume measurement occurs with the degree of classification of the resin particles and the presence or absence of jarring during the settling period. Standard measurements are normally taken after backwash classification followed by free settling.

In theoretical work it is frequently more desirable to know the volume and weight of the resin phase alone rather than the total settled volume. This has been measured by sucking the resin dry on a Büchner funnel, by air drying just to the point of free-flowing granules or by wiping the beads with an absorbent material; but probably the most rigorous of all methods is the centrifugal method in a closed vessel proposed by Gregor (29). In any case, the beads are finally weighed directly for wet resin weight or immersed in a known volume of water to obtain wet resin volume.

The volume occupied by the ion exchange resins is dependent, other factors remaining the same, on the ionic form of the resin. This is controlled primarily by the two factors, ionic size, including water of hydration, and

degree of ionization of the resin in the given form. Each of the primary resin types has been investigated in this respect, although as with almost all of the more fundamental studies, the bulk of the work has been with the sulfonated styrene type of resin. The reasons for this are obvious: (a) monofunctionality, (b) reproducible dry weight capacity (c) essential uniformity throughout structure, (d) rapid exchange rates, (e) relatively simple structure, and (f) wide usage.

Gregor, Gutoff & Bregman (28) have shown this swelling for a large number of cations of the sulfonated styrene type of exchanger at 8 per cent cross-linkage. A few of these volumes, expressed in slightly different form, are indicated in Table II in which the sodium form volume is arbitrarily chosen as 100 per cent.

TABLE II
WATER-SWELLING OF SULFONATED STYRENE—8 PER CENT DVB

Form	Volume (percentage)	Form	Volume (percentage)
Silver	85	Sodium	100
Potassium	96	Magnesium	103
Calcium	97	Hydrogen	107
Ammonium	99	Tetramethyl Ammonium	114

Though the approaches have been somewhat different, Pepper (58), Bauman (1), and Glueckauf (22) have all shown similar results with this resin type.

Wheaton & Bauman (77) have reported on similar swelling studies with a strong base anion exchanger containing 7.5 per cent crosslinkage. In this case the chloride form was arbitrarily chosen at 100 per cent.

TABLE III
WATER SWELLING OF QUATERNARY AMINE TYPE ANION EXCHANGER STYRENE—
7.5 PER CENT DVB

Form	Volume (percentage)	Form	Volume (percentage)
Iodide	90	Sulfate	103
Bromide	95	Carbonate	106
Nitrate	95	Hydroxide	108
Chloride	100	Fluoride	113

With the weak base and weak acid types of anion and cation exchangers the volumes occupied by the various monovalent ionic forms are in the same sequence as described above except for the hydroxyl and hydrogen forms. Above about 10 pH for weak anion exchangers and below about 4 pH for

weak cation exchangers, the resins are very slightly ionized and occupy much less volume than the salt forms. For example, Gregor (23) shows for a certain carboxylic type exchanger a 71 per cent volume increase with 50 per cent conversion from hydrogen form to sodium form and a 103 per cent volume increase on complete conversion. Kunin & Barry (45) showed by implication the same effect in reporting that the exchange rates of the salt forms of another carboxylic acid type resin are much faster than those of its slightly dissociated acid form.

The effect of ionic concentration on resin volume has been reported by a number of authors for various resin types (1, 28, 58, 77, 78). This effect is readily apparent from work of Gregor *et al.* (28), interpreted in Table IV, which shows the decrease of volume for the ammonium form of a sulfonated styrene type (9 per cent crosslinked) resin in ammonium chloride solutions of increasing concentration.

TABLE IV
SWELLING OF SULFONATED STYRENE—8 PER CENT DVB IN SALT SOLUTION

NH ₄ Cl molality	Settled volume (percentage)
0.01	100 (arbitrary basis)
0.12	99
0.61	98
1.23	95
3.34	91
7.12	87

Volume changes with crosslinkage can be very great, of far greater magnitude than the factors just reported, for the volumes that may be occupied by the ionized resins approach infinity as crosslinkage approaches zero, i.e. a poly electrolyte in the usual sense.

This factor has been investigated for the sulfonic type cation exchangers

TABLE V
EFFECT OF CROSS-LINKING ON SWELLING OF SULFONATED STYRENE—DVB

Percentage DVB	V _s
0.4	42.40
2	4.602
4	2.757
8	1.618
10	1.436
13	1.302
17	1.195
26	1.115

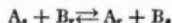
by Reichenberg, Pepper & McCauley (59), Gregor *et al.* (28), and Bauman (1). The anion exchangers have been similarly studied by Kunin & Myers (48) and Wheaton & Bauman (77).

The volume of the hydrogen form of the sulfonated styrene type resin is indicated in Table V (28) in which crosslinkage is indicated by percentage divinylbenzene (DVB). V_s = volume occupied by 1 g. of dry hydrogen form resin on equilibrating in water.

ION SELECTIVITY

When immersed in a solution containing more than one type of ion, all of these ions compete for the ionic groups in the resin. There have been many attempts to apply the law of mass action to this ion exchange process with varying degrees of success. Though in general such studies have failed to account fully for the data observed, the selectivity coefficients obtained from such an approach are of real value in ion exchange applications.

The selectivity coefficient for the exchange reaction



is usually expressed as

$$K_B^A = \frac{[A_r] \cdot [B_s] \cdot f_{B_s}}{[B_r] \cdot [A_s] \cdot f_{A_s}}$$

where $[A_r]$ and $[B_r]$ are the amounts of ions A and B in the resin phase, $[B_s]$ and $[A_s]$ are their concentrations in the solution, and f_{B_s} and f_{A_s} are the activity coefficients in solution. As has been pointed out many times this definition ignores the activities of the ions in the resin phase, there being no method of determining these quantities at present.

The selectivity is normally measured by immersing a known weight of resin in one ionic form in a known volume of a solution of the other ion of known concentration. The mixture is agitated in a constant temperature bath until equilibrium is attained. Both resin and solution phases are then analyzed for the two ions. The phases may be separated by the centrifugal method. Satisfactory results are frequently achieved by analyzing the liquid phase only and assuming stoichiometric exchange, though care must be used where the liquid volume is small relative to the resin volume because of the inequality of electrolyte concentration in the two phases (2). In some cases a molecular adsorption has been shown to occur also, and this may be a factor in the results for weakly ionized electrolytes.

Dynamic methods have also been used successfully for the determination of selectivity coefficients. In this method a solution containing A and B ions in known concentrations is passed through a tower filled with resin in either the pure A or the pure B form until the effluent concentrations are equal to the influent. The final resin composition may then be analyzed and checked against the analysis of the total effluent. Repeat runs with varying ratios of A and B in the influent can then be made to cover the range of resin compositions. A comparison of static and dynamic methods is given by Duncan & Lister (15).

The early investigators were most concerned with the dependence of the classical equilibrium constant on the temperature and total concentration of the contacting solution. However, it was not long before the equilibrium constant was found to vary appreciably with another property of the system, namely the proportion of the exchanger's capacity which is occupied by each of the competing ions, and the case arose of an "equilibrium constant" which is constantly changing throughout the course of the exchange reaction. As a result K_B^A has been renamed the selectivity coefficient and has little meaning unless accompanied by the corresponding state of the resin, usually denoted by X_A , the fraction of the resin in the A ion form at equilibrium.

The most extensive study has been in the case of the uni-univalent exchange on a resin of the sulfonated cross-linked polystyrene type. Such systems investigated either on commercial resins or comparable laboratory products include $\text{Na}^+ - \text{H}^+$ (15, 26, 51, 59), $\text{K}^+ - \text{H}^+$ (12, 26), $\text{NH}_4^+ - \text{H}^+$ (12, 50), $\text{Ag}^+ - \text{H}^+$ (32, 50), $\text{Ti}^+ - \text{H}^+$ (50), $\text{K}^+ - \text{Na}^+$ (26), $\text{K}^+ - \text{NH}_4^+$ (26), $\text{K}^+ - \text{Li}^+$ (26), and $\text{K}^+ - \text{R}_4\text{N}^+$ (26) where R_4N^+ has been tetramethylammonium, tetraethylammonium, tetra-*n*-butylammonium, and trimethylphenylammonium. In uni-univalent exchanges the selectivity coefficient is largely independent of total concentration changes in solutions less than 1*N* (2), and varies only slightly with temperature. Although there have been differences of opinion on the shape of the curve when K_B^A versus X_A is plotted, there has been fairly general agreement on the order of magnitude of the values obtained. $K_{\text{H}^+}^{\text{Na}^+}$ versus X_{Na^+} appears to give a rather flat curve with $K_{\text{H}^+}^{\text{Na}^+}$ varying between 1.5 and 2.0 with a maximum at approximately $X_{\text{Na}^+} = 0.4$. $K_{\text{H}^+}^{\text{K}^+}$ appears to be only slightly higher and about the same as $K_{\text{H}^+}^{\text{NH}_4^+}$. Gregor & Bregman (26) give values of $K_{\text{Na}^+}^{\text{K}^+} = 1.60$ at $X_{\text{K}^+} = 0.58$ and $K_{\text{NH}_4^+}^{\text{K}^+} = 1.10$ at $X_{\text{K}^+} = 0.52$. Lithium appears to be less selectively held with a $K_{\text{Li}^+}^{\text{K}^+}$ value of 2.66 at $X_{\text{Li}^+} = 0.74$. In general the selectivity decreases as the hydrated size of the ion increases. However, Gregor & Bregman (26) have shown that in the case of organic tetraammonium ions, and particularly in the case of trimethylphenyl ammonium, this decreased selectivity is somewhat offset by adsorption effects resulting from the similar organic nature of the ion and resin. The system $\text{Ag}^+ - \text{H}^+$ has been extensively studied by Högfeldt, Ekedahl & Sillen (32). $K_{\text{H}^+}^{\text{Ag}^+}$ was found to vary with X_{Ag^+} , increasing approximately linearly from 9 to 11 as X_{Ag^+} increased from 0.1 to 0.9. It was independent of the concentration of the solution and particle size of the resin. They were able to approach the equilibrium from either side to obtain K values which agreed within experimental accuracy. Other workers (50) have reported adsorption effects in this system and in the $\text{Ti}^+ - \text{H}^+$ system which interfere with the asymmetry of equilibrium.

Reichenberg, Pepper & McCauley (59) and Gregor & Bregman (26) have recently investigated the effect of the relative cross-linking of a sulfonated polystyrene resin on its selectivity in uni-univalent exchanges. They have shown that as the cross-linking, or divinylbenzene content, of the resin approaches zero, the resin loses its selectivity, and K approaches one for univalent ion pairs. Not only does K deviate from one with increasing cross-

linkage but even the shape of the K versus X curve may be completely altered. In the $\text{Na}^+ - \text{H}^+$ system Reichenberg, *et al.* have shown the curve develops from a linear nearly horizontal line, through a curve showing a flat maximum, to a case in which $K_{\text{H}^+ \text{Na}^+}$ is continuously decreasing with increasing X_{Na^+} as the divinylbenzene content is increased from 2 per cent to 33 per cent.

This dependence of selectivity on cross-linking may account for some of the discrepancies occurring among different workers measuring selectivity coefficients. While the polystyrene-divinylbenzene base resins offer a very convenient way of building in any desired amount of crosslinkage, there are no accurate ways of assuring either an exactly known ratio of styrene and divinylbenzene in the final polymer or their completely homogeneous distribution. Furthermore, there are no methods available at present for measuring the amount of crosslinking in the finished resin except the approximate methods of measuring the water content or the volume changes which occur in the resin when it is taken from one form to another.

Among the uni-divalent and uni-trivalent exchanges for which equilibrium data have been presented are $\text{Ca}^{++} - \text{H}^+$ (50, 51), $\text{Ba}^{++} - \text{H}^+$ (14, 51), $\text{Ni}^{++} - \text{H}^+$ (50), $\text{Ce}^{+++} - \text{H}^+$ (51), and $\text{La}^{+++} - \text{H}^+$ (12). The introduction of a multi-valent ion into the mass-law expression introduces mathematical complications that have been treated in a variety of ways by the various investigators. Although there is considerable discrepancy among the data presented on any one system, the order of magnitude of $K_{\text{B}^{A^{++}}}$ appears to be at least 10 to 20 times that of $K_{\text{H}^+ \text{K}^+}$ at equivalent total concentrations of the order of 0.1 N . The selective coefficient in such exchanges has been shown to be a function of X_A as in the uni-univalent exchanges. While the total ionic concentration was a minor variable in uni-univalent exchanges, it has a pronounced effect in uni-divalent exchanges, $K_{\text{B}^{A^{++}}}$ increasing as the concentration decreases (2). No data has so far been presented on the effect of the degree of cross-linking on $K_{\text{B}^{A^{++}}}$. The selectivity coefficients in uni-divalent, uni-trivalent and di-trivalent should be worthy of further extensive investigation, both because of the general lack of agreement in the field at present and the usefulness of such equilibrium data in the water-softening and industrial applications fields.

Kunin & Myers (47) have studied a weak-base exchanger and found its selectivity for various anions dependent upon the pH and total concentration of the solution, the structure and valency of the anion, and the ionization constant of the corresponding acid.

Although the exchange equilibrium on strongly basic anion exchangers has not been extensively studied, (46, 77) a number of the generalizations made above for the strong acid cation exchanger appear to hold true in this case also. The selectivity coefficient is dependent on the state of the resin, its divinylbenzene content, and, at least in the case of uni-divalent exchanges, on the total concentration. No data have been presented on the variation of K with temperature. Wheaton & Bauman (77) have presented lists of the selectivity coefficients for various monovalent anions of two such

resins. The order of the selectivities for the halides in both cases is in agreement with the order of their decreasing hydrated diameters. The high selectivity shown for dichlorophenate and salicylate ions can be accounted for on the basis of adsorption due to their organic character. It is of interest to note that the order of the selectivity series is dependent upon the nature of the organic radicals in the quaternary ammonium grouping of the resin.

If the failure of different workers to obtain substantiating data in the determination of cation exchange selectivity coefficients can be traced to variations between the different samples of resin used, such discrepancies should be even more evident in future data presented on anion exchangers. Besides the uncertainties of structure introduced in the polymerization stage, the subsequent reactions in the preparation of anion exchangers are less predictable than that of sulfonation.

DENSITY

A direct pycnometric determination of a centrifuged resin sample suffices for the accurate evaluation of the density of a water wet sample of resin. The comparable pycnometric determination for the dry resin upon immersion in water is complicated by the lack of volume additivity of resin and water (comparable to that of sodium chloride plus water). The use of a solvent, such as *n*-octane, which does not swell the resin has been suggested and used satisfactorily (28).

RATE OF EXCHANGE

Both static and dynamic methods have been used for the determination of ion exchange rates. The rates for most exchange reactions of small ions is so rapid (99 per cent in 1 to 2 min.) even for the largest stable particles of exchange resins that static methods are usually very inaccurate. The static method consists of adding resin in one ionic form to a solution containing the second ion, agitating rapidly, and extracting at intervals small portions of the solution for analysis. In some cases a recording of the pH, conductivity, density, refractive index, color, or electrode potential of the electrolyte may be made continuously to follow the exchange reaction.

Of greater utility are the dynamic methods in which the solution is run through a bed of the resin. Deep beds may be used and an analysis made of the slope of the breakthrough curve determined. Alternately, rates may be determined with a very shallow bed operated at high flow rates with an analysis of the initial leakage of the ion being exchanged. These dynamic methods are particularly suitable since exchange rates are frequently dependent upon the degree of turbulence in the solution and at the resin-liquid interface, and the dynamic methods duplicate the practical bed operation more closely than the static methods.

SCREENING EFFECT OF IONS

The reported screening effect of ions based on their size and a given resin

network is largely a rate-controlled process, though with some of the larger ions the selectivity seems to be very real.

Gregor *et al.* (25) have studied a number of ions of increasing size and their behavior with various cross-linked sulfonated polystyrene resins. With the ions studied they showed that all but tetrabutylammonium ions were absorbed up to the resin's capacity after several days, even with a resin 36 per cent cross-linked. The percentage of capacity attained in 6 hr. with these various resins has been determined approximately from a graph and is tabulated in Table VI. Kunin & Myers (48) have made somewhat different

TABLE VI
CAPACITIES OF SULFONATED STYRENE RESINS FOR SEVERAL CATIONS
(After Six Hours Equilibration)*

Ion	6 Per Cent DVB	17 Per Cent DVB	36 Per Cent DVB
Potassium	100	100	100
Tetramethylammonium	100	100	100
Trimethylphenylammonium	100	100	70
Tetrabutylammonium	70	40	15

* All capacities expressed in percentage.

studies, using larger anionic groups with both strong and weak base anion exchangers. They showed in both cases that, though the resin capacity decreased somewhat with increase in crosslinkage, ultimate capacity for the large anion decreased much more rapidly. This is indicated in Table VII showing absorption of penicillin on a strong base resin. Capacities are in milliequivalents per dry gram.

TABLE VII
STRONG BASE RESIN PENICILLIN CAPACITY VERSUS CROSSLINKAGE

Relative Crosslinking	Total Capacity	Penicillin Capacity
1	3.2	3.2
2	3.1	2.6
3	3.1	2.3
4	2.9	1.8
8	2.6	0.1

Another indication of this screening effect has been reported by Bodamer & Kunin (5) in which it is shown that the catalytic inversion of sucrose with the acid form of a sulfonated styrene type resin increases with lowered crosslinkage. This is presumably related to the ability of the sucrose and invert products to move in and out of the resin structure.

Richardson (60, 61) has shown that small contaminating salts may be

readily separated from the relatively large sulfonic type cotton dyes. He reports that ions above 30 Å in size are effectively prevented from entering, and being absorbed by, a weak base anion exchange resin.

MOLECULAR ADSORPTION

Many of the early observations on the behavior of ion exchange materials in the removal of ions from solution were attributed to adsorption in capillary pores of the resin or to a competitive adsorption between separate ions. Likewise the removal of acids from solution by a weakly basic anion exchange resin has been attributed to adsorption rather than ion exchange. With increasing knowledge of the nature and the number of exchange groups in the synthetic organic exchange resins it has been possible to show that the exchange of ions is stoichiometric and that the total exchange power for ions is measured exactly by the number of exchange groups in the resin. Under these conditions exchange equilibria are more reasonably interpreted as a mass action exchange of ions between resin and aqueous phases rather than as adsorption, even though equivalent mathematical equations may be derived through Freundlich adsorption isotherms.

A number of investigators have now shown that the exchange resins do show, in addition to their exchange power, a marked capacity for the adsorption of neutral molecules. Possibly the first observation of such adsorption was made in the removal of colored bodies in the demineralization of beet sugar solutions, and a great deal of commercial work has been directed toward the preparation of porous exchange resins combining a maximum of such adsorption power with suitable exchange capacity. The naturally-occurring colored compounds are so numerous and complex, however, that quantitative studies and a clear-cut separation between adsorption and exchange effects have been difficult to achieve.

Some excellent experimental work on the adsorption of acids and bases on cation exchange resins has been done under reproducible conditions by Davies, Erler & Gregor. Davies & Thomas (13) studied both carboxylic and sulfonic resins of the phenolic type and showed that appreciable adsorption of aliphatic carboxylic acids, increasing with increasing chain length, and a very marked adsorption of aromatic carboxylic acids occurred. The sulfonic resins were also shown to adsorb pyridine and ammonia over and above their exchange capacity for these bases. Erler's (16) work confirms the adsorption of the aliphatic carboxylic acids and shows that dibasic acids are adsorbed less than monobasic acids. Gregor, Collins & Pope (27) have shown that a sulfonic acid cation exchange resin will selectively adsorb such neutral molecules as urea, methyl acetate, ethyl acetate, and isobutyl acetate and have studied such variables as the ionic form of the resin, the temperature, and polar and nonpolar concentrations.

ION EXCHANGE SEPARATIONS ENHANCED BY COMPLEX FORMATION

In his ion exchange review Boyd (6) stated

... it is now possible to separate every element ... which forms an ion in solution

from every other such element by proper employment of the techniques of ion exchange chromatography

The formation of complex ions with vastly different behavior with respect to a given exchanger continues to broaden the possibilities for ion separations, in many cases turning a difficult separation into a relatively simple one. The first indication of the importance of complex formation relative to rare earth separations dates back to the work of Tompkins, Khym & Cohn (75) in which yttrium, europium, praseodymium, cerium, and lanthanum were separated on a sulfonated styrene type cation exchange resin using buffered citric acid solutions as elutriants. By adjustment of pH, the formation of various citrate complexes can be controlled almost at will. This technique, then applied to a great number of separations, led to the isolation of several new elements and enabled the preparation of large quantities of the pure rare earth elements. Spedding (70) has recently reviewed the rare earths and their separation by ion exchange methods. Complexing agents other than citric acid, but similar in that they contain multiple carboxylic groups, have recently been introduced. Fitch & Russell (17) have shown the utility of iminodiacetic acid and nitrilotriacetic acid, reporting increased stability of the iminodiacetic acid complexes with greater atomic number in the rare earth series.

Prominent in recent literature have been separations of the type in which ionic complexes are formed in solution prior to passage through the exchange column. This principle, however, was investigated several years earlier by Sussman, Nachod & Wood (73) in which anion exchange resins were useful in the recovery of metals as their common anion complexes, e.g., chromium as chromate. This technique was applied to chromium, gold, iron, molybdenum, palladium, platinum, and vanadium. Present available anion resins would greatly facilitate these operations. Kraus & Moore (40, 41, 42) have recently prepared a series of papers showing the utility of forming metal anion complexes in accomplishing selective adsorption on strongly basic anion exchange resins. In their work, separations have been made at low pH in high chloride or chloride-fluoride concentrations. For example, ferric iron, of the more common metal ions, forms a series of complex ferric chloride anions (FeCl_4^-) dependent on chloride ion concentration and low pH, which are extremely tightly held by a strongly basic anion exchanger but which are decomposed and very readily eluted from the resin column with water.

As has been shown many times in ion exchange chromatography, the use of radioactive tracers are very useful in the analyses of the ion exchange column and effluent at any given time during a run. In their studies of ferric iron behavior, Kraus & Moore (40) used Fe^{59} in hydrochloric acid solutions of increasing concentration and showed that resin adsorption by the strong base anion resin was correspondingly increased. By comparison, aluminum and the rare-earth ions were practically unadsorbed. A solution of 30 p.p.m. iron in 2 *M* AlCl_3 and 3 *M* HCl was essentially freed of iron by passage through the resin. Teicher & Gordon (74) have investigated this separation of ferric iron from aluminum as an analytical method. This type of behavior

has most recently been applied by Kraus & Moore (42) to separations of zirconium and niobium and of niobium, tantalum, and protactinium. Similarly Huffman & Lilly (34) have investigated and reported the separation of hafnium and zirconium, present in HCl-HF mixtures. Huffman, Iddings & Lilly (33) have shown separations of zirconium, hafnium, niobium, and tantalum. In this case separations were in hydrochloric acid, and it is interesting to note that the order of elution of zirconium and hafnium is reverse to that described by Kraus & Moore for fluo-ions (40). Huffman & Oswalt (35) had somewhat earlier described the separation of promethium and europium in tracer quantities by development of their citrate complexes on an anion exchange column.

Nor has the use of complexing agents been limited to those of the metals. Khym & Zill (39) have, by use of a strongly basic anion exchange resin and sugar borate complexes, reported very fine separations of the monosaccharides—fructose, glucose, mannose, and galactose. By somewhat similar behavior Zager & Doody (81) have removed glycerol from aqueous solutions as a glycerol borate complex anion. In this case no practical regeneration technique has been found. Gabrielson & Samuelson (20), in a series of articles on the use of ion exchangers as analytical tools, described a very novel modification of the bisulfite addition reaction in which the bisulfite form of a strongly basic anion exchange resin is used to remove quantitatively aldehydes and ketones from solution. Regeneration is readily accomplished by elution with sodium bicarbonate solution.

Mills & Dickinson (56) showed that reduced copper and silver amine complexes of weakly basic anion exchange resins were very excellent for removal of dissolved oxygen from water, to less than 0.1 p.p.m.

The importance of formation of fluosilicate ions in deionization work was shown by Bauman, Eichhorn & Wirth (3). In this case a fluoride such as calcium fluoride is added to the water prior to passage through a cation exchange bed. The resultant hydrofluoric acid then reacts with the very weak silicic acid to form the strong fluosilicic acid which is readily removed with a weak base anion exchanger. The advent of the strong base anion resins has removed the general desirability of this method.

CATALYSIS

Strongly acid cation exchange resins of the sulfonated styrene-divinylbenzene type possess an internal acid concentration equivalent to that in 20 per cent hydrochloric acid solution so that they may be expected to show marked catalytic power in any acid-catalyzed reaction. Oddly enough, this catalytic effect was first observed as a detrimental effect in the demineralization of sucrose solutions, where an undesirable inversion to glucose and fructose occurs in the acidic cation exchanger if the temperature is not reduced. Indeed, this problem has become more and more severe as higher exchange capacity resins have been developed. Recently, however, the catalysis has actually been used to advantage in the production of invert sugar (4).

A number of investigators have studied the rate of hydrolysis of esters in the presence of strongly acidic cation exchange resins, even to the extent of using such resins as the packing in continuous hydrolysis columns. The majority of the fundamental work has been carried out in agitated batch reactors, but an interesting study on a steady state continuous tower reactor has recently been presented by Saletan & White (62). The batch work has indicated a major surface catalytic effect of the resin, whereas Saletan & White find excellent correlation with a mass catalytic effect with the rate controlled by diffusion of the components in the resin phase. Hammett & Bernhard (30) conclude that surface reaction is controlling on the basis of the catalysis of the hydrolysis of long-chain esters and on the relatively rapid catalysis of a resin containing exchange groups only at the surface of the particles; but their work also shows a marked variation of the catalytic effect with the extent of crosslinking of the resin, which indicates a mass diffusion control.

Sulfonic acid cation exchangers have also been shown to be active catalysts in the hydration of olefins (43), the dehydration of alcohols (72), acetal synthesis and alcoholysis (72), ester alcoholysis (30, 62), and the formation of uronosides (57). Anion exchange resins have been used as catalysts in the conversion of nicotinonitrile to nicotinamide (21) and the Knoevenagel condensation between aldehydes and esters (82).

ION EXCHANGE AS A TOOL IN STUDY OF ELECTROLYTES

The equilibrium of a cation exchange resin with an electrolyte solution is dependent upon the ratio of the activities of the cations in the solution. Thus the cationic content of a particular cation exchange material should be the same when equilibrated with any solution containing equal cation activity ratios. A method is hereby furnished for the comparison of activities in one solution with those in a second solution; and if the second solution is extremely dilute, the activity ratios in the first solution are obtainable directly. Thermodynamically, the only requirement is that the resin remain in the same state when in contact with the two solutions. This criterion may be expected to hold true in dilute solutions because of the exclusion of anions from the cation resin phase and because of the constancy of resin volume with changing electrolyte concentration. At higher electrolyte concentrations the resin phase composition will change, and exact activity ratios will no longer be attained; though this limit may be pushed to higher concentrations through the use of resins of higher cross-linking.

A second method for the determination of ion activities by means of exchange resins involves the use of radioactive tracers. At very low relative concentrations of one cation in a mixed electrolyte, a linear relationship is obtained between the concentration of electrolyte in the resin and solution phases. Relative activities of an ion in the presence and absence of complexing agents are then very easily obtained by equilibrating the solutions with an exchange resin and determining the ion concentration in the resin phase by direct counting of radioactivity. These radioactive methods are so sensi-

tive that a range of 10^5 in concentration may readily be covered while maintaining a linear distribution isotherm between resin and solution phases.

Considering the versatile power of this new tool for the study of even complex electrolyte mixtures, it is rather surprising that so little use has been made of it. Vanselow (76) appears to have been the first to realize this utility when he applied the base-exchange reaction of bentonite clays to the determination of activity coefficients of mixed electrolytes. Recently three papers have appeared by Schubert (64) and Schubert and co-workers (65, 66) on the determination of the activities of radium, zirconium, niobium, and barium in solutions of their complex salts. Connick & Mayer (11) have recently published a similar study on cerous complexes. Fronaeus (19) has studied the copper acetate complexes.

ION EXCHANGE MEMBRANES

For many years it has been known that natural membranes, such as those surrounding living cells, show a high selectivity for transfer of cations over anions or vice versa, and even in many cases a marked selectivity for one cation or anion over another. When solutions of different concentrations are separated by such membranes, a differential potential is developed. The first extensive work on this phenomenon was carried out by Michaelis and co-workers (55) using untreated collodion membranes. Sollner (67, 68) and his group have since greatly extended this work. They have proved that the development of a potential across the membrane depends upon the nature, concentration, and positions of the electrically charged groups which are a part of the membrane, that is, upon its ion exchange characteristics. Cation permeable membranes were produced by the oxidation of the collodion to give carboxy groups and anion permeable membranes by the adsorption of protamine in the collodion. Such membranes are fairly rugged, are practically impermeable to ions of like charge at concentrations below .01 *N* and under favorable circumstances will show a potential difference approaching the theoretical Nernst potential: $E = RT/NF \ln C_1/C_2$, about 59 mv. at room temperature for a tenfold concentration gradient. Their main shortcomings are the weak basic or acidic nature of the electroactive groups, which makes the membranes sensitive to pH, and the low concentrations of such groups in the pores of the membranes, which reduces the ionic selectivity at higher solution concentrations. Theoretical Nernst potentials have therefore only been obtained in solutions 0.1 *N* or less. Recently Sollner & Neihof (69) have published a note describing a strong acid type membrane made by incorporating sulphonated polystyrene in collodion. Potentials obtained with this membrane were somewhat better in more concentrated solutions and especially in acid solutions.

A very similar line of work has been carried out by Marshall (52, 53) and co-workers using mineral membranes made either by shaping plates from crystalline zeolitic materials or by evaporation of colloidal clays. Under some conditions they have obtained potentials in agreement with those predicted and have studied the use of such membranes for the determination of sodium,

potassium, ammonium, calcium, and magnesium ion activities in colloidal solutions. However, these membranes are also sensitive to pH and are limited to concentrations below 0.1 *N* and with some ions to below 0.004 *N*.

The next step forward in ion-exchange membrane development came with the work of Wyllie & Patnode (80) and as a result of the membrane characteristics of shale strata in the earth (79). The membrane progressed from small shale barriers to ground shale or clay bonded in neutral resin and finally to a membrane of ground commercial sulphonic type cation exchange resin bonded in methylmethacrylate or polystyrene. Though these membranes had high electrical resistance, theoretical potential differences could be obtained at concentrations as high as 3 *N* NaCl. The possibilities of using such membranes as sodium indicating electrodes were examined.

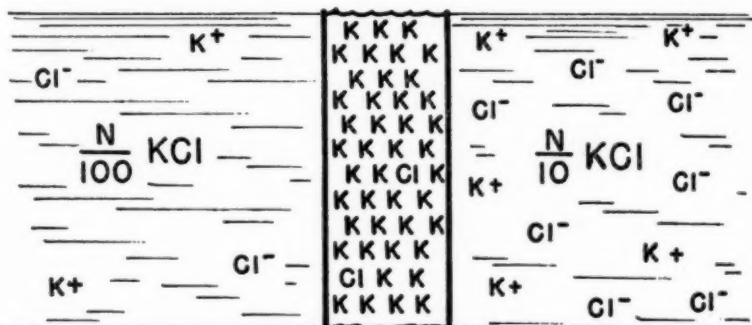


FIG. 2

The development of exchange resins in sheet and rod forms has been carried on in this country by Juda and co-workers and in England by Kressman and co-workers. Although little has been published concerning these materials, both groups have announced the availability of various homogeneous membranes, both cationic and anionic, and either unmounted or with various backings to improve mechanical strength (8, 10, 37, 44). These homogeneous membranes show extremely high electrical conductivity, in some cases approaching that of an equal volume of strong electrolyte, and excellent selectivity especially at low salt concentrations.

Permselective membranes promise to extend markedly the usefulness of exchange materials, so that a discussion of their fundamental characteristics may be helpful. Consider the case of a cation exchange film separating two solutions of KCl, one 0.1 *N* and the second 0.01 *N* (Fig. 2). A high capacity cation exchange resin will contain an internal concentration of potassium greater than 5 *N* and a chloride concentration of less than 0.01 *N* under the conditions of Figure 2 (2). This represents a ratio of K⁺/Cl⁻ of greater than 500:1, and in favorable circumstances this ratio may become over 1000:1. Assuming equal mobilities of K⁺ and Cl⁻, the transference of current through

such a membrane will be practically completely through the K^+ , as shown experimentally by Jenny (36).³ Likewise, the diffusion of K^+ from the 0.1 *N* KCl to the 0.01 *N* will be rapid compared to that of the chloride ion, so that a net positive charge is built up in the left cell containing 0.01 *N* KCl. In similar fashion an anion exchange membrane carries electrical current almost exclusively on the wings of the anions and will build up an equal potential but of opposite sign. Thus a series of alternating cation and anion exchange membranes separating alternate weak and strong electrolyte concentrations will form a battery, as shown in Figure 3. Such a battery (for concentration differentials of tenfold) can theoretically build up 59 mv. per compartment, or 5.9 v. for 100 compartments, a potential sufficient to electrolyze KCl, or to light a flashlight bulb if taken off with reversible electrodes. The same system may be used in reverse to concentrate or demineralize electrolyte solutions by means of electrical power.

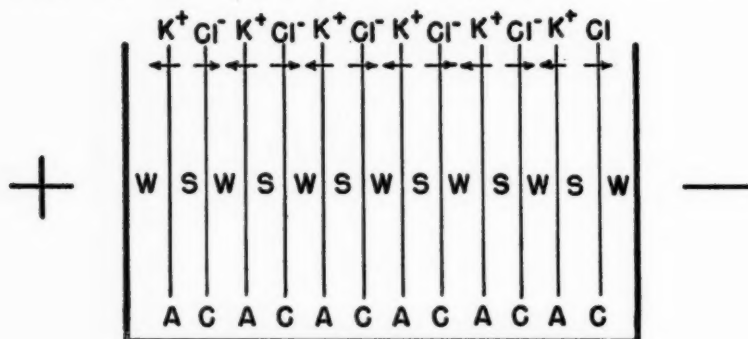


FIG. 3

At high electrolyte concentration the exclusion of chloride by cation exchange membranes becomes less effective, so that the transference numbers of cation and anion become more nearly equal in the membrane. This effect occurs at lower electrolyte concentrations for exchange membranes of lower exchange capacity, so that high volume capacity is desirable for high selectivity. A secondary effect in the system shown in Figure 3 is the diffusion of water from the dilute to the concentrated solution causing concentration equalization without adding to the potential of the system. This solvent diffusion relative to the ion diffusion is also minimized by high volume exchange capacity. Hence both effects require high crosslinking in the resin membrane, but the slower diffusion rates at high crosslinking requires a

³ Although Jenny's layer of cation exchange resin held in place by two uncharged casings was not strictly a continuous membrane, it behaved as one at low solution concentrations. In a KCl solution Jenny found that at solution activities of 0.04, 0.10, 0.22 and 0.60 the transference number of the chloride ion was 0.09, 0.15, 0.25, and 0.34 respectively.

compromise in the choice of the extent of crosslinking. These considerations are almost identical with those for granular exchange resins.

As discussed above, an ion exchange membrane transfers current almost exclusively through migration of the exchangeable ions, positive ions for cation exchangers and negative ions for anion exchangers. A packed bed of exchange resin behaves exactly like a continuous membrane when the solution phase is sufficiently dilute (36).

The removal of Na^+ from a cation exchange resin by electrolytic regeneration was studied by Spiegler & Coryell (71). As indicated in Figure 4 a flow of high conductivity water was maintained to rinse out the sodium hydroxide, hydrogen, and oxygen formed by electrolysis. As electrolysis proceeded, the wave front between $R-Na$ and $R-H$ moved to the left, and this movement was followed by radioactive tracer techniques. The method was suggested as a means of regenerating exchange resins without regenerant chemicals.

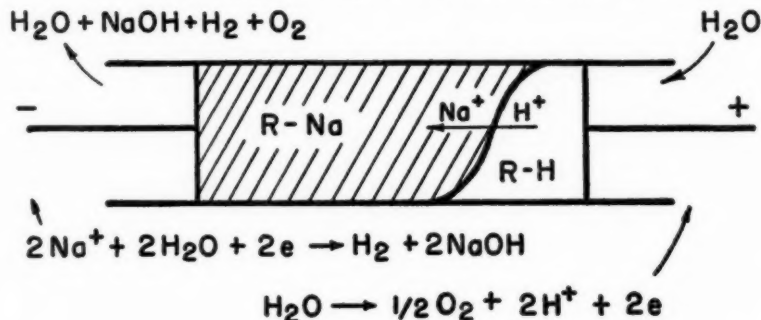


FIG. 4

A similar method has been used by Kakihana & Yasima (38) for the chromatographic separation of Cu^{++} and Co^{++} ions. In this case the Cu^{++} and Co^{++} ions were driven by electrolysis down through a column of resin in the hydrogen form and were separated in 60 hr.

Applications of membranes to the measurement and control of electrolyte concentrations by potentiometric means, as diaphragms in electrolytic cells (18), to the concentration of dilute electrolytes, to the demineralization of aqueous solutions and emulsions of organic compounds, to the development of power, to the separation of similar ions (18), etc. open up many new possibilities for ion exchange materials.

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THERMOCHEMISTRY AND THE THERMODYNAMIC PROPERTIES OF SUBSTANCES¹

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A noteworthy recent development in this field has been the appearance of a great interest in the thermodynamics of irreversible processes. This interest has culminated in the appearance of a new book on the subject by de Groot (1) reviewed by MacDougall (2). Haase (3, 4) has also rather thoroughly treated the general principles in a work which was in press at the time de Groot's book appeared. Both authors lay great stress on Onsager's principle of reciprocity. De Groot, Jansen & Mazur (5, 6) have discussed the mechanocaloric effect, and Holtan (7) has discussed a number of processes, both papers using Onsager's principle. Holtan has discussed thermocells in particular, and has criticized the assumptions of Eastman and co-workers (8), who have reported measurements on a number of thermocells, from which they have calculated "absolute ionic entropies." Their results are also criticized by Tyrrell & Hollis (9), who point out that they are inconsistent with the expected Soret coefficient. Dickel (10), has discussed thoroughly the efficiency of the diffusion processes for separation of isotopes.

Three papers should be of special interest to teachers of thermodynamics. Crawford (11) has discussed the peculiar thermodynamic behavior of heat absorbed, and work done by a process, and expresses changes in these quantities in terms of differentials along the chosen path. After choice of path, they become functions of a single variable. Simon (12) has discussed and amplified Nernst's arguments concerning the logical foundations for the third law, and Frost (13) has represented oxidation states by plotting the free energy of the state, in electron volts, versus the oxidation state.

DATA OF STATE FOR GASES, LIQUIDS AND SOLIDS

Generalized equations of state and empirical equations are discussed by Chu & Chin (14), Benson & Golding (15), Wentorf *et al.* (16), and Ivanov (17). Maslan & Aberth (18), have found that the theory of deBoer and Lunbeck does not apply well to eight liquids which they examined. Duclaux (19) has expressed the second virial coefficient in a form convenient for application to a gas thermometer, and Ito (20), has applied an equation of state to entropy of vaporization. The correlation of the virial coefficients with intermolecular forces has been discussed by Epstein & Roe (21), Hamann (22), Kihara (23), Kikuchi (24), Moelwyn-Hughes (25), and Rowlinson (26, 27). Rushbrooke & Scoins (28) and Hart, Wallis & Pode (29) have developed virial coefficients in terms of the superposition principle of Kirkwood and

¹ The survey of the literature pertaining to this review was concluded in December, 1951.

Boggs. Compressibility data, sometimes accompanied by virial coefficients or thermodynamic properties, have been reported by: Michels *et al.* (30, 31), and Tsiklis (32), A and N₂; Beattie *et al.* (33, 34), Xe; Kendall & Sage (35), CO₂; Oliver *et al.* (36), C₂ClF₃; O'Brien & Alford (37), CS₂; Canjar *et al.* (38), propylene; Baxendale *et al.* (39); and Riediger (40), C₆H₆; Reid & Smith (41), C₂H₅OH. Reported compressibility data for mixtures are: Michels *et al.* (42), H₂—N₂—NH₃; Benedict *et al.* (43), heptane and eleven hydrocarbons of lower molecular weight; Eduljee *et al.* (44), hexane—heptane—octane; and Newitt & Weale (45), binary mixtures of water, acetone and eight chlorine-substituted hydrocarbons.

The critical state.—Four papers deal with the interesting question of the existence of a true critical point, instead of a critical region. Attack & Schneider (46), have studied the coexistence curve of SF₆ in the critical region and are uncertain as to the existence of a flat portion of the curve; Rowden & Rice (47), from a study of the critical solution curve of cyclohexane—*aniline*, conclude that there is a flat portion. Zimm (48), has concluded from statistical, mechanical, and mathematical arguments that, at the critical point, the derivatives of fugacity or pressure with respect to density, of every order, must be zero, and hence that Mayer's argument of the implausibility of satisfying all the necessary conditions at a single point is invalid. Mayer (49) does not retract his former position but admits "... it seems ... at the present time, that it [Zimm's argument] is at least as plausible as the argument advanced previously [by Mayer] ...". The reviewer is pleased to note that one is still entitled to believe in the classical critical point.

Other critical data and discussions are: Price (50), second order transitions and critical points; Curtiss *et al.* (51), velocity of sound and Joule-Thomson coefficient at critical point; Michels & Strijland (52), heat capacity of CO₂ near the critical point; Oliver *et al.* (53), C₇F₁₆; Hoge & Lassiter (54), H₂, D₂, and HD; and White, Friedman & Johnston (55), N₂. Some critical constants of hydrogen isotopes also occur under vapor pressures (57, 58, 59).

Vapor pressures.—References dealing with vapor pressures of inorganic substances are: Clark *et al.* jointly with Michels *et al.* (56), A; Hoge & Arnold (57), Friedman *et al.* (58, 59), and Grilly (60), isotopic hydrogen molecules; Hall (61), Au; Johnston and co-workers (62, 63, 64, 65), Co, Ta, V, and Zr; Clark *et al.* (66), H₂S; Miller *et al.* (67), SF₆; Kabesh & Nyholm (68), SnCl₄, SnBr₄, and SnI₄; Fairbrother & Frith (69), NbF₅ and TaF₅; Michels & Wassenaar (70), Xe; and Vance & Whitman (71), Zn. Those dealing with organic compounds are: Charnley & Skinner (72), methyl and ethyl mercuric halides; Michels & Wassenaar (73), C₂H₄; Beattie *et al.* (74, 75), normal pentane and neopentane; Kay & Warzel (76), 2,2,4-trimethylpentane (iso-octane); Potter & Saylor (77), *o*-, *m*- and *p*-fluorotoluene, benzotrifluoride and the *o*-, *m*- and *p*-chloroderivatives, and *p*-bis-(trifluoromethyl)-benzene; Smith & Bonner (78), acetaldehyde, propionaldehyde and *n*-butyraldehyde; Balson & Adam (79), lewisite; Bolling *et al.* (80), morpholine; Bright (81), biphenyl, bibenzyl, and diphenylmethane; Hopke & Sears (82),

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three picolines and *p*-di-*tert*-butylbenzene; McEwan & Rigg (83), tetrazole and the 1,5- and 2,5-diphenyl derivatives; and Nicolini (84), *n*-pentane, methylcyclohexane, iso-octane, 2,2-dimethylbutane, isopropyl ether, diethyl acetal, dimethyl acetal, diethyl formal and dimethyl formal.

HELIUM

Pomeranchuk (85, 86) has calculated by statistical mechanics the effect of impurities on the properties of He II and the expected properties of pure He³, for different postulates. Duclaux (87, 88) has set up equations from which he concludes that the λ -point cannot be a triple point, and, from the change of vapor pressure with temperature combined with the heat of vaporization of He in the neighborhood of the λ -point, he calculates values for Pv/RT . From the change of Pv/RT with temperature and pressure, he concludes that He exists in two modifications, not only in the liquid, but also in the gaseous, state. De Groot *et al.* (89) have applied the thermodynamics of irreversible processes to the behavior of He II, assuming it a mixture of normal and superfluid kinds. Gorter *et al.* (90) have calculated the specific heats and entropies of He II from available measurements, and have discussed the results on the basis of the two fluid model.

Heat-capacity measurements have been made of liquid He near 1°K. by Hull *et al.* (91), and of He adsorbed on rutile, which shows a shift corresponding to the λ -point, by Mastrangelo & Aston (92). Long & Meyer (93) have measured the vapor pressure at the λ -point, and Essl'son *et al.* (94) have measured the vapor pressure over solutions of He³ in He⁴.

THERMODYNAMICS OF SURFACES AND ADSORBED PHASES

Hill, Emmett & Joyner, and Hill (95, 96) have pointed out that the thermodynamic quantities usually obtained for adsorption processes are the differential quantities, but that the integral quantities are generally desirable for statistical mechanical correlation. Using Brunauer-Emmett-Teller (BET) theory, they have expressed the relations of integral thermodynamic properties in terms of the measured differential ones, and, from measured adsorption isotherms of nitrogen on Graphon (a partially graphitized carbon black), have calculated the corresponding integral values. Aston and co-workers (97, 98, 99) have studied the heat of adsorption of nitrogen on titanium dioxide, and find the BET theory inadequate to represent their results. Kemball & Schreiner (100) have found that the quotient a_1b_2/a_2b_1 of the BET theory must range from 10^{-5} to 10 from case to case. Morrison and co-workers (101, 102) have measured the heat capacity, integral heat of adsorption, and entropy of argon on titanium dioxide.

Studies have been reported on the heats of adsorption of H₂ on Ni and Fe (103); N₂ on an iron catalyst (104); CO and H₂ on a zinc oxide-chromium oxide mixture (105); water vapor on carbon (106) and on BaSO₄ (107); butyl alcohol (108), and some hydrocarbons (109) on carbon; and some aliphatic amines on silica gel (110). Young (111) has calculated the heat of adsorption of argon on KCl, and Eley (112) has correlated heat of adsorption

with covalent bond energies. Hansen (113) and Whittton & Young (114) have reported on general relations of thermodynamics to adsorption.

Hill (115) has calculated the variation in density from bulk liquid to gas. The greater part of the change occurs within about three molecular diameters. Benson & Shuttleworth (116) and Choate & Lune (117) have calculated the change of surface energy with size of nucleus or hole, and Mackor (118) has given a theoretical discussion of the stability of dispersions in hydrocarbons. Jasper & Mayer (119, 120) have reported the effect of temperature on interfacial tensions of water against some esters of monochloroacetic and monobromoacetic acids.

THERMODYNAMICS OF POLYMERS

Flory and co-workers (121, 122, 123, 124, 125) have correlated intrinsic viscosity of solutions of polymers with effective hydrodynamic radius, which in turn is correlated to root-mean-square distance from end to end of polymer chain. Intramolecular interactions of segments of the chain will cause the length to be different from that expected in the absence of such interaction, and this expansion factor is correlated with the free energy, enthalpy, and energy of mixing with solvent.

Bartenev (126) has discussed the equation of state of rubber, and Garner *et al.* (127) have correlated the free energy increase of systems of soaps with the subjection of the systems to stress. Measurements have been reported on the osmotic pressure of cellulose nitrate solutions by Meerson & Lipatov (128), the energy of dilution of polyvinyl acetate solutions by Meares (129), and the partial molal free energy of polyvinyl alcohol-acetate copolymer solutions by Nord *et al.* (130). Mathot (131) has reviewed thermodynamic studies of polymeric systems.

THERMODYNAMICS OF SOLUTIONS

Interest continues in the general theory of solutions. Because of the overlap with the fields of other chapters in this Review, only brief note will be made of a few papers. Guggenheim & McGlashan (132) have extended their treatment to the consideration of next-nearest neighbors, and Prigogine & Garikian (133) have extended the method of Lennard-Jones and Devonshire to include effect of change in vibrational frequency of molecules in the mean field of their neighbors. McGlashan (134) has discussed the entropy of mixing of molecules of single and double size, and van der Waals (135, 136) has correlated measurements on hydrocarbon pairs of approximately single and double size, with theory. Longuet-Higgins and co-workers (137, 138) have continued development of the theory of conformal solutions, and have applied it to carbon dioxide-ethylene mixtures. Bonnor (139) has developed a formula for the electrostatic energy of molecules in solutions, and has correlated it with solutions of water in alcohols, and alcohol in heptane, but Müller (140) has attempted to correlate thermodynamic properties with dielectric properties, apparently without success. Staveley, Johns & Moore (141) have measured the solubility and heat of solution of water in benzene

mixed with several alcohols, and have correlated their observations with interactions between hydroxyl groups and polarizable benzene molecules. Durham & Hawkins (142) have calculated the heat of mixing, and the relative activity coefficients for solid solutions KBr—KCl, RbBr—RbCl, KCl—RbCl, and KBr—RbBr. Bell (143) has reviewed the thermodynamics of solutions.

Vapor-liquid equilibria.—Prahl (144) has presented a simple empirical formula, containing three adjustable constants, for expressing the composition of vapor in terms of liquid composition. Experimental determinations of vapor-liquid equilibria for inorganic systems are: Michels *et al.* (145), $\text{NH}_3\text{—H}_2\text{—N}_2$; Sebba (146), $\text{AsCl}_3\text{—GeCl}_4$; Shair & Schurig (147), $\text{SbF}_5\text{—HF}$; Barber & Cady (148), $\text{WF}_6\text{—perfluoro-}n\text{-pentane}$; and Rohrback & Cady (149), $\text{WF}_6\text{—perfluorocyclopentane}$.

Reports for systems in which one of the constituents is water are: Zernike (150), ammonium bicarbonate; Sanders & Young (151), ammonium nitrate and ammonia; Fontana (152), phosphoric acids; Johnson & Molstad (153), and Gokcen (154), lithium chloride; Culberson & McKetta (155), methane; Dunning, Evans & Taylor (156), sucrose; and Huff, McBain & Brady (157), some detergents.

Liquid-vapor equilibria for organic systems are: Othmer *et al.* (158), ethyl alcohol—water; Aroyan & Katz (159), hydrogen—*n*-butane; Haselden *et al.* (160), $\text{CO}_2\text{—ethylene}$, and $\text{CO}_2\text{—propylene}$; Reamer, Sage & Lacey (161, 162, 163), $\text{CO}_2\text{—propane}$, $\text{CH}_4\text{—H}_2\text{S}$, and $\text{CH}_4\text{—}n\text{-butane}$; Elbishlawi & Spencer (164), $\text{CH}_4\text{—benzene}$ and $\text{CH}_4\text{—toluene}$; Banderet (165), benzene with pentatriacontane and pentatriacontadiene; and Sieg, Crützen & Jost (166) benzene—1,2-dichloroethane. Baxendale *et al.* (39), Brown & Ewald (167), and Crützen, Haase & Sieg (168), have given data on liquid-vapor equilibria for benzene—biphenyl, benzene—heptane, and *n*-heptane with cyclohexane and methylcyclohexane, respectively. In addition, the excess free energy, enthalpy, and entropy are given by these authors. Additional references for organic systems are: Benedict *et al.* (169), twelve hydrocarbon mixtures; Ebert *et al.* (170), aniline—hexane, aniline—cyclohexane and 2,2'-dichloroethyl ether—methylcyclohexane; Kretschmer & Wiebe (171), propane and the butanes in ethanol; Sieg, Crutzen & Jost (172), methanol—*n*-butyl acetate; Kieffer & Grabiell (173), 2-ethoxyethanol with alkyl benzenes; Amick *et al.* (174), methyl ethyl ketone—*sec*-butyl alcohol; Karr *et al.* (175), acetone—chloroform—methyl isobutyl ketone; and Moeller *et al.* (176), ethyl ether—ethyl alcohol—water.

Activity coefficients and ion exchange resins.—The chief thermodynamic application of ion-exchange resins has been in determining activity coefficients. Gregor (177) has developed a theory of exchange resins by use of the Gibbs-Donnan equilibrium. Lowen *et al.* (178) have reported concentration equilibrium quotients for eight systems on Dowex 50 involving the ions Na^+ , H^+ , NH_4^+ , Ag^+ , Ti^+ , Ni^{++} , and Ca^{++} , and Connick & Mayer (179) have measured relative activity coefficients of cerous ion, using Dowex 50, primarily to determine the extent of complexing. Schubert (180) has measured

the activity coefficient of $\text{Ba}(\text{NO}_3)_2$ in uranyl nitrate, with Amberlite IR-1.

Semenchenko (181) has developed a number of inequalities relating activity coefficients and mole fractions in binary systems. Prigogine & Desmyter (182), have determined activity coefficients in solutions of *tert*-butyl alcohol in CS_2 , CCl_4 , and cyclohexane, and found, by spectroscopic measurement of the OH vibration band, that deviations from ideality can be ascribed to complex molecule formation.

Additional reports on activity coefficients or activities are: Elving and co-workers (183, 184, 185), binary systems involving *cis*- and *trans*-dichloroethylene with methanol, methylal, tetrahydrofuran, isopropyl ether, ethyl formate, methyl acetate, acetone, and 2-butanone; Callow (186), PbO-SiO_2 ; Hall (187), Au-Cu ; Elliott & Chipman (188, 189), Cd in Pb, Sn, Bi, and Sb and in Pb-Bi, Pb-Sb, and Pb-Sn; Wagner (190), Hg in Li-Tl, Na-Tl, and Na-K; and Sedlet & DeVries (191), NaCl and KCl in liquid ammonia. Reports for aqueous systems are: Hayes & Martin (192), $\text{Mn}(\text{IO}_3)_2$; Nicholson & Felsing (193), the perchlorates of the alkaline earth metals and of magnesium; Otake (194), thallium picrate; and Crockford & Sakhnovsky (195), HCl in aqueous D-fructose.

NEW THERMODYNAMIC DATA

Heats of formation and of combustion.—Heats of formation and of combustion are not separated because in nearly all reports of combustion, the heat of formation is also given, and in the few other cases, it can be easily calculated.

Tatevskii *et al.* (196) have correlated the heats of formation of 44 alkanes by an equation containing nine constants, Kapustinskii & Golutvin (197) have correlated heats of formation of various compounds with atomic numbers and atomic radii, and Dyatkina (198) has discussed the resonance energies of hydrocarbons. Cartledge (199) has extended his correlations of heats of formation with what he has called the ionic potential, namely the ionic charge divided by ionic radius.

Experimental determination of heats of formation of inorganic compounds are: Brewer & Searcy (200), AlO and Al_2O ; Holley & Huber (201), MgO and Al_2O_3 ; Oketani & Maebashi (202), Al-Mg alloys; Rulon & Mason (203), $\text{Al}(\text{BH}_4)_3$; Lohr & Cunningham (204), AlCl_3 , LaCl_3 , and PrCl_3 ; Eastman *et al.* (205), oxide-sulfides of Ce, Zr, Th, and U; King (207), silicates of Ca and Zn; Siemonsen (208), BeCl_2 , CaCl_2 , SrCl_2 , BaCl_2 , and AlCl_3 ; Kazarnovskaya & Kazarnovskii (209), KO_2 ; Ketchen & Wallach (210) and McKisson & Bromley (211), Na-K alloys; Humphrey (212, 213), Ti_3O_5 , TiO_2 , TiN , and TiC .

Hartley, Pritchard & Skinner (214), have reported HgR_2 and HgRX , with R=ethyl and phenyl, and X=Cl, Br and I, and Tanaka *et al.* (215) have given results on five organosilicon compounds.

The heats of combustion of organic compounds, generally also with the heats of formation are: Knowlton & Prosen (216), C_2N_2 ; McEwan & Rigg (83), 28 compounds related to tetrazole; Parks & Vaughan (217), biphenyl; Cole & Gilbert (218), *p*-nitroaniline, hydrazobenzene, 4,4'-dinitrohydrazo-

benzene, and hippuric acid; Prosen, Maron & Rossini (219), ten C_4 hydrocarbons; Breitenbach & Derkosch (220), some polystyrenes and peroxides and anhydrides of several organic acids; Cottrell & Gill (221), nitrates of the three methylamines, glycine, and four other amines; Casey & Fordham (222), ethyl chloride; Serijan & Wise (223), some diphenyl- and dicyclohexyl-pentanes and hexanes; Roberts & Jessup (224), α -methyl styrene and four fractions of its polymers; Hormats & Van Artsdalen (225), neopentyl radical. Szwarc (226) has reviewed the heats of formation of hydrocarbon radicals.

Heats of dissociation and bond energies.—Reported heats of dissociation and bond energies are: Hultdt & Lagervist (227), BeO, MgO, CaO, SrO, BaO; Kistiakowsky *et al.* (228), N_2 ; Brewer *et al.* (229), N_2 and C_2N_2 ; Pannetier & Gaydon (230), NH; Doescher (231) and Eucken & Wicke (232), F_2 ; Gelles (233), some oxygen-halogen bonds; Field (234), C—H in CH_2 ; Szwarc *et al.* (235, 236, 237, 238), C—Br in halogenated methanes, and in substituted benzyl bromides; Brown *et al.* (239), B—N in trimethyl boron compounds amines; Glazer & Alexander (240), N—H...O hydrogen bond in substituted ureas. Voevodskii (241) has given an empirical equation for C—H and C—C bonds in saturated hydrocarbons and aliphatic radicals. Glockler (242) has reviewed the bond energies of hydrocarbons.

Heats of solution and of reaction.—Simons & Blum (243) have calculated heats of formation of solid solutions of KBr—KCl from the solid salts. Measured heats are: Coulter & Monchick (244), Li in NH_3 ; Mulder with Schmidt (245), some guanidine salts, KNH_2 , KI, KCNS, NH_4CNS in NH_3 ; Dimmling & Lange (246), the propyl alcohols in water; Van Artsdalen & Anderson (247), B_2O_3 and H_3BO_3 in H_2O ; Awtry & Connick (248), $I_2^- = I_2 + I^-$; Ketchen & Wallace (249), $Na + H_2O = Na^+ + OH^- + 1/2H_2$, $K + H_2O = K^+ +$ etc.; Peppler & Newman (250), ZnO in HCl(aq); Westrum & Eyring (251), Am in HCl(aq); Yatsimirskii & Astasheva (252), crystalline complexes of ethylene diamine with Ni and Cd halides reacting with HCl(aq); Westrum & Wallmann (253), $PuF_3(s) = PuF_3(g)$.

Heat contents and heat capacities.—Heat capacities which have been measured to sufficiently low temperatures, and from which entropies have been calculated, will be found under *Entropies* (p. 138). While heat contents are given in only some of the references listed, no essential division need be made, since heat content relative to an arbitrarily chosen temperature can always be found from the heat capacities, except when transitions occur within the interval of interest.

Giulotto & Loinger (254) have found good agreement between calculated and experimental heat capacity of calcite from 0 to 150°K. Parkinson, Simon & Spedding (255) have found anomalies in the heat capacities of La, Ce, Pr, and Nd. They explain the high values as the result of free electronic heat capacity. Anomalies caused by different types of transitions, sometimes magnetic, have been found: Coughlin, King & Bonnickson (256), FeO, Fe_2O_3 , and Fe_3O_4 ; Fakidov & Grazhdankina (257), ferromagnetic chromium sulfide; Shirane & Sawaguchi (258), lead titanate; Sawada, Ando & Nomura (259), tungsten oxide; Jaffray & Lyand (260), V_2O_5 .

Other inorganic heat capacities reported are: Ginnings, Douglas & Ball

(261), Be; Foley & Giguère (262), H_2O_2 ; Douglas, Ball & Ginnings (263), Hg; Lander (264), SrO , BaO , CaO , $BaCO_3$, and $SrCO_3$; Blomeke & Ziegler (265), La_2O_3 , Pr_6O_{11} , and Nd_2O_3 ; Coughlin (266), $NiCl_2$; Christy & Lawson (267), $AgBr$; and McCready (268), sodium silicate solutions.

For organic compounds the reported heat capacities are: Barrow (269), seven octanes in the vapor state; McCullough, Person & Spitzer (270), cyclohexane and four dimethylcyclohexanes; von Ueberreiter & Nens (271), distyrene and a polystyrene; Weltner & Pitzer (272), CH_3OH ; Douglas, Ball & Torgesen (273), glucose; and Sage and co-workers (274, 275, 276), *n*-hexane methylcyclopentane, *n*-octane, ethylenediamine, furfuryl alcohol, isopropylamine, methyl alcohol, nitromethane, the hydrazine-water system, and the furfuryl alcohol-aniline system.

Entropies.—Reports and discussions of entropies of mixing appear under the heading Thermodynamics of Solutions. Powell & Latimer (277, 278) have given formulas correlating entropies of solids, and of aqueous solutes, with mass, charge, and ionic radius. Oriani (279) has subdivided the entropy of melting into that coming from expansion, and the remainder, which is attributed to disorder. Bernstein & Burns (280) have discussed the correlation of entropy and the potential barrier to rotation in N_2O_4 , and Pitzer (281) and Aston (282) have reviewed the problem of hindered rotation in hydrocarbons. Hugus (283) has pointed out that the value for cuprous ion appearing in the Selected Values of Chemical Thermodynamic Properties (1949) is unreasonable, and has calculated another value, and Wagman (284) has acknowledged the error, and made a recalculation in substantial agreement with Hugus. Bonnemay (285) has calculated the change in entropy for oxidation of Zn to Zn^{++} , and Staveley & Tupman (286) have compiled entropies of vaporization for 53 liquids.

Entropies from low-temperature heat capacities have been reported as follows: Egan *et al.* (287, 288), hydroxyapatite and fluorapatite; Grisard, Bernhardt & Oliver (289), ClF_3 ; Johnston and co-workers (290, 291, 292, 293, 294, 295), B, decaborane, Cu_2O , *o*- D_2 , Li_2O and Zr; Todd and co-workers (296, 297, 298), calcium and zinc silicates, $FeCl_3$, and FeO , MnO and VO ; Kelly & Snyder (299), $NaOH$; Oliver and co-workers (300, 36), C_7F_{16} and C_2ClF_3 ; Furukawa *et al.* (301, 302), benzoic acid and diphenyl ether.

Entropies from low-temperature heat capacities together with those obtained from spectroscopic data are: Barrow & McClellan (303), naphthalene; Scott *et al.* (304, 305), 2-methylbutane, 2,3-dimethylbutane and 2-thiabutane (methyl ethyl sulfide); Aston and co-workers (306, 307), methylhydrazine and dimethylhydrazine.

Thermodynamic values, particularly entropies, calculated from spectroscopic data and other sources of molecular properties are: Decker, El-Sabbah, and Voelz, each with Meister & Cleveland (308, 309, 310), CF_4 , CHF_3 , CDF_3 and $CClF_3$, 1,1,1-trichloroethane, and SiF_4 ; Ichishima & Mizushima (311), C_6H_6 ; Klein, Cleveland & Meister (312), O_3 ; Lippincott & Lord (313), cyclooctatetraene; Godnev *et al.* (314), C_6H_5Cl ; Gilles & Wheatley (315), Ti; Madigan & Cleveland (316), CCl_4 and $CHCl_3$; and Pulford & Walsh (317), $NOCl$.

Thermodynamic data from equilibrium measurements and electromotive force data.—Equilibria involving vapors and solutions are entered in the section Thermodynamics of Solutions, and ionic equilibria may be found in the chapter, "Solutions of Electrolytes."

Elliott (318) has given a general discussion of thermodynamic equilibrium, and Tatevskii (319) has developed two methods of calculating the equilibrium constant for isotope exchange reactions. Braune, Peter & Neveling (320) have reinvestigated the dissociation of sulfur vapor, apparently with great care, and find excellent agreement between calculations and their observations, if they assume that S_4 is an important constituent of the vapor. Russell, Martin & Cochran (321) have measured the equilibrium between $AlCl_3$, Al and $AlCl$. Other measurements of inorganic equilibria are: Lander (264), dissociation of $BaCO_3$ and $SrCO_3$; Galinker & Korobkov (322), water vapor with $NaOH-H_2O$ and $KOH-H_2O$; Rosenquist (323), CaS , H_2O , CaO , and H_2S ; Chiche & Dode (324), dissociation of CuO and Cu_2O ; Hood & Woyski (325), HCl and HF with chlorides and fluorides of Na, Ba, Ni, and Pb; Matoba & Unotaro (326), and Alcock & Richardson (327), FeS , H_2 , Fe , and H_2S ; Sudo (328), metal and H_2S to H_2 and metal sulfide, metals Fe, Ag, and Pb; Gregory (329), dissociation of $FeBrCl_2$; McQuillan (330), hydrogen—titanium; Mallett & Campbell (331), hydrogen—thorium; and Rezhukhina *et al.* (332, 333, 334), equilibria involving hydrogen and the tungstates of Fe, Mn, and Co. Dunning & Nutt (335), have attempted to express the equilibria involved in the dissociation of liquid nitric acid.

Equilibria involving organic substances are: Taylor (336), dissociation of acetic acid vapor; Vergoz (337), equilibrium in condensation of $NH_2 \cdot (CH_2)_{10} \cdot CO_2H$; Howlett (338), *tert*-butyl chloride, isobutene and HCl ; Bonner (339), α - and β -D-glucose pentaacetates; Bezzi & Ilceto (340), formaldehyde and polymers in water; and Browning & Emmett (341) equilibrium $CH_4 = C + 2H_2$, with C formed by decomposition of Fe_3C . Niemann and co-workers (342 to 348), by ingenious use of rate studies, have found the dissociation "constant" for several enzyme-substrate, and enzyme-inhibitor complexes.

Oxidation potentials are reported by Connick & McVey (349) for $Pu(III)$ — $Pu(IV)$, and by Rulfs & Elving (350) for several oxidation states of rhenium. Saegusa (351, 352) has studied the thermodynamic properties of $CdCO_3$, K_2CO_3 , and Na_2CO_3 by use of cells involving cadmium amalgam, $CdCO_3$, and Ag, Ag_2CO_3 electrodes. Raikhinshtein (353) has reported on the dependence of the potential of bromide—bromate mixtures on the concentration of hydrochloric acid, and Goates *et al.* (354) have calculated the thermodynamic properties of Ag_2S from the cell Ag , Ag_2S , H_2S , HCl — HCl , H_2 , Pt.

MISCELLANEOUS TOPICS

New methods.—Buzzell & Sturtevant (355) have described twin calorimeters for slow-heat evolution, with reaction in one, electric heat in the other (if reaction is exothermic). Resistance thermometer output is amplified, used to control heater. Potential across the heater is squared and supplied to an

integrator. Thomas (356) designed a calorimeter for slow processes, similar in principle to the ice calorimeter, but using naphthalene. Schulze (357) has described a simple and sensitive calorimeter for heats of mixing, and has reported heat of mixing for $C_6H_6-CCl_4$, and alcohol with chlorobenzene, bromobenzene, and toluene. Magnus & Becker (358), and Sunner & Bjellerup (359), have described combustion calorimeters. Nathan (360) has given a method for measuring the heat capacity of metals, and Los & Morrison (361) describe the calibration of resistance thermometers at low temperatures.

Vapor pressures have been measured by Dainton & Kimberly (362), using radioactive tracers, and by Teckner & Lossing (363), using the mass spectrograph. Brady, Huff & McBain (364), have replaced thermocouples and galvanometer by two thermistors, in apparatus for measurement of vapor pressure. Other vapor-pressure apparatus is described by Dauphinee (365), Johnson & Molstad (153), and Klages & Möhler (366).

Wise & Altman (367) have used a critical-flow orifice to obtain mean molecular weight, and from it, the chemical equilibrium in $NO_2-N_2O_4$ mixture.

The use of digital computers for chemical calculations has been discussed by Brough *et al.* (368), and by Martin & Yachter (369). Pennington & Kobe (370) have shown the use of numerical integration, and Davidson & Fuller (371) have described an electrical analogue computer for thermodynamic calculations. Dreisbach (372) has illustrated the accurate use of the Ramsay-Young and Dühring rules for vapor pressures.

Electricity and magnetism.—Smith-White (373) has given the energy of a dielectric in an electrostatic field, Mackor (374) has discussed the thermodynamics of the double layer on silver iodide and mercury, and Levine & Suddaby (375, 376) have derived formulas for the free energy of electrical double layers. Shaposhnikov (377), Garrett (378), and Dolecek (379), have discussed the theory of spin-spin relaxation in paramagnetic substances, the relation of entropy and free energy to intensity of magnetization in an anti-ferromagnetic crystal, and the magnetism of superconductors, respectively.

Phase transitions of the second kind.—Sokolov (380) in a general mathematical discussion of such phase transitions finds them analogous to a Curie point, and Sokolov & Shmidt (381) have correlated the anomalous heat capacity of barium titanate with the electric field of spontaneous polarization. Semenchenko (382) and Semenchenko & Skripov (383) have measured the heat capacity of trimethylamine-water mixtures in the neighborhood of the critical solution temperature, and find it similar to the λ -point of helium. Urazovskii & Voronov (384) have pointed out that many of the effects of phase transitions of the second kind could be explained by the change of equilibrium with temperature of a chemical transformation of the molecules.

Propellants.—Penner (385), Campbell (386), and Crepin & Levy (387), have discussed in general problems of interest, and Bredt (388) and Barr & Wilson (389) have calculated the thermodynamic properties of hydrogen,

and of the stoichiometric mixture of hydrazine and hydrogen peroxide, respectively.²

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BOND ENERGIES AND BOND DISTANCES¹

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INTRODUCTION

This review covers the years of 1950 and 1951, although some earlier work will be mentioned in order to give the trend of development. Both bond energies and bond dissociation energies will be dealt with as well as bond distances. Early compilations of bond energies were made by Pauling (88), Wheland (135), Skinner (104), and lately by Pitzer (92), Glockler (51), Syrkin & Dyatkina (109), and Nebbia (86). It is interesting to note that the present topic was the subject of three scientific meetings during the two-year period. The Royal Society (London, March, 1950) held a meeting on bond energies and bond lengths. The Faraday Society (Oxford, April, 1951) devoted its Discussions Meeting to the subject of hydrocarbons, covering their structure and bond properties, their reactions and their oxidation. One of the symposia of the American Chemical Society (New York, September, 1951) gave its attention to the subject of bond strengths. These meetings indicate the great interest that exists at this time in this branch of physical chemistry.

THE ROYAL SOCIETY MEETING

A brief report by Longuet-Higgins (74) appeared in *Nature*. At this meeting Evans (34) discussed the difference in meaning of the terms "bond energy" and "bond dissociation energy." He pointed out for example that the bond energy of the oxygen-oxygen bond in hydrogen peroxide is 33 or 52 kcal. depending on the oxygen-hydrogen bond energy taken from the water molecule or the hydroxyl ion. He suggested strongly that bond dissociation energies, being directly measurable quantities, are more important. The fact that they differ in different molecules for the rupture of the same bond actually gives valuable information about resonance energies and promotion energies in the various molecules or atoms concerned. He mentioned the case of mercury dimethyl, where the energies needed to remove the first and second methyl groups are 50 and 8 kcal. respectively. This difference is due to the loss in energy which the mercury atom suffers as it changes from the divalent triplet state to the normal ground state. Szwarc (112) reported on the experimental methods for the measurement of bond dissociation energies and the heats of formation of radicals. Factors affecting bond energies of diatomic molecules were considered by Walsh (133). He discussed the

¹ The survey of the literature pertaining to this review was concluded in December, 1951.

experimental determination and the theoretical significance of the concept of electronegativity and suggested that the bond energy of the bond A—H and hence the stretching force constant be taken as a measure of this quantity. Since the electronegativity is also related to the ionization potential there should be a smooth relationship between the force constant and the ionization potential of the atom A. In polyatomic molecules the electronegativity of a multivalent atom must depend on its state of hybridization. Warhurst (134) discussed the description of the chemical bond in terms of resonance between ionic and covalent structures and the concept of ionic character first developed by Pauling (88). He states that the theory of ionic-covalent resonance in single bonds involves assumptions incapable of proof from first principles and that it rests largely on the successful interpretation of a variety of experimental results. The theory has been successfully applied to ionic resonance energies in terms of the electronegativity concept, to the dipole moments of simple halides and hydrides, to bond contractions relative to the covalent radius sum and the dependence of force constants upon the dielectric constant of the molecular environment. It is hoped that it would be possible to reformulate the theory of ionic-covalent resonance in such a way that its many successes could be more easily understood in terms of fundamental principles. However, the continued critical use of the theory seems justified since there is at present no alternative method of equal generality.

Cottrell & Sutton (19) made calculations on a number of idealized molecules, hoping to obtain a clearer understanding of the dependence of bond energy on nuclear charge in diatomic molecules. The Heitler-London-Sugiura wave mechanical treatment is extended to systems of two nuclei and two electrons [nuclear charges greater or less than the proton charge ($+e$) and not necessarily equal in magnitude]. It is found that the transfer of positive charge between initially equal nuclei leads to an increase of the purely covalent part of the bond energy, resulting largely from the decreased internuclear repulsion and independent of any ionic character of the bond. These results make it possible to reconcile Pauling's adjacent charge rule (88) with Gordy's (54, 55) rule connecting electronegativities and bond energies. It appears that the covalent energy of heteropolar molecules is much greater than that given by the arithmetic or geometric mean rule (88). The question of ionic-homopolar resonance was also discussed critically by Coulson (20). He mentioned some of the theoretical difficulties which include our ignorance of fundamental energies and of the orbitals used. Care is required in the use of the conventional theory in the case of hybrids because the atomic radius and the effective electronegativity of a hybrid depend on the degree of mixing of the basic atomic orbitals. There are further difficulties associated with the independence, partial delocalization, and possible bent character of the bonds. Some suggestions for future work are the study of pairing schemes, the theoretical evaluation of covalent bond energies, the relation between hybridization and ionic resonance, the conditions favoring *p*- and *d*-hybridization and the repulsions between inner and valence electrons.

While the five papers just reviewed considered mainly σ bonds, the second set of five discussions dealt with σ - π bonds. Lennard-Jones (70) traced the concept of the π bond from its early days when it was introduced to account for the torsional rigidity of the ethylene molecule and the paramagnetism of oxygen. The π bond forms the basis of the theoretical treatment of many of the properties of organic molecules. It has been possible to make extensive calculations of resonance energies and bond lengths. The assumption has to be made that the resonance integral between adjacent atomic orbitals is a simple function of the distance between the atoms involved. The percentage double bond character and the lengths of carbon-carbon bonds have been calculated for many molecules and have been found in good agreement with x-ray results. Coulson's bond order-bond length curve has been used successfully for predicting carbon-carbon distances in many unsaturated hydrocarbon molecules. However, for heterocyclic molecules the theory is not satisfactory. All that can be claimed for such molecules, is that calculations indicate trends. The theory of heteromolecular conjugated systems is one of the major outstanding problems. The present position of bond lengths in conjugated molecules was surveyed by Coulson (21). He explained that in molecules containing σ - π bonds it is assumed that the σ and π electrons can be treated separately. The first are presumably localized. The wave function and the energy of the π electrons are obtained by the valence bond method or by the method of molecular orbitals in terms of exchange and resonance integrals. In general it is necessary to use the concept of fractional bond order, and this procedure is sound. Several possible refinements of the theory are mentioned, as for example how the extent of hybridization will affect bond lengths and that in heteromolecules a self-consistent field may have to be introduced. Certain improvements can very likely be made in bond length calculations: for example, allowance can be made for bond length changes caused by repulsion between neighboring charges and mutual polarization of the atoms, taking care of the variations of the resonance integral resulting from unequal bond lengths. At present it is possible to predict bond lengths to better than 0.015 Å in hydrocarbon molecules and 0.03 Å in heteromolecules.

In a paper on x-ray measurements of bond lengths in planar aromatic hydrocarbons, Robertson (97) reported studies on pyrene ($C_{16}H_{10}$), coronene ($C_{24}H_{12}$), and ovalene ($C_{32}H_{14}$). The measured values are compared with Coulson's molecular orbital calculations. On the whole, the agreement is most encouraging. The measured bond lengths for pyrene are probably good to 0.03 Å, and the average discrepancy between observed and calculated values is 0.022 Å. For coronene and ovalene, the estimated experimental error is only 0.01 to 0.02 Å and the difference between theory and experiment amounts to only 0.013 Å, which is as good as can be expected. Naphthalene and anthracene were also studied, and the bond lengths are correct to better than 0.01 Å. The central bond in naphthalene appears to be shorter than calculated. The same bond is very much shorter than its counterpart in anthracene. The amount of this difference is difficult to explain on any

theory. The theoretical values were calculated by Daudel & Daudel (25) and Vroelant & Daudel (130). New bond order-bond length relationships were presented by Cox & Jeffrey (24) for the carbon-nitrogen and carbon-sulfur bonds which can be used to correlate theoretical calculations with experimental measurements. As in carbon-carbon bonds, considerations of π bonding only account for much of the data of lengths intermediate between single and double bonds and the effects of hyperconjugation, polarity, hybridization, and other environmental factors appear to be very small. The situation with regard to carbon-oxygen bonds is unsatisfactory and demands more experimental and theoretical work.

Unimolecular dissociations are usually divided into two classes: homolytic dissociations ($X:Y \rightarrow X\cdot + Y\cdot$) and heterolytic dissociations ($X:Y \rightarrow X: + Y:$). Longuet-Higgins (75) considered the latter where X or Y is a conjugated system. The effect of substitution in X or Y on the energy of such a reaction can be calculated simply by a combination of molecular orbital and first order perturbation theory. The results are encouraging when applied to recent data on the ionization constants of heteroaromatic amines by Albert, Goldacre & Phillips (1). The theory also accounts for the observed reactivity of methyl groups in certain positions in heteroaromatic molecules and predictions are made for the reactivity of the methyl groups attached to the biphenylene ring system. Further predictions concern the effect of nuclear substitution on the activity of an aromatic system toward electrophilic and nucleophilic reagents.

THE FARADAY SOCIETY DISCUSSIONS

In his introductory paper Evans (35) again stressed bond dissociation energies (D), their relation to activation energies (ΔE) for certain types of reactions ($\Delta E = \alpha \Delta D$), definition of resonance energy, alkyl radicals and steric factors and configurations in hydrocarbons. Lennard-Jones & Pople (72) delivered a quantum mechanical discussion on the factors responsible for molecular shape and bond energies. It is shown that a satisfactory qualitative picture of the structure of a molecule can be obtained by considering only electrostatic repulsions and the antisymmetry principle. The same theoretical considerations are applied by Lennard-Jones & Hall (71) to the calculation of ionization potentials of hydrocarbons and the discussion of their energies. Estimates of bond energies of carbon-carbon and carbon-hydrogen bonds, based on 170 kcal. for the heat of sublimation of carbon, were presented by Glockler (52). The ionization potentials and heats of formation of *sec*-propyl radical, $D(\text{sec}-C_3H_7-H) = 4.07$ ev, and of *tert*-butyl radical, $D(\text{tert}-C_4H_9-H) = 3.88$ ev, were reported by Stevenson (107) from mass spectroscopic measurements. Similar studies on methane and methyl cyanide lead McDowell & Warren (79) to support 120 kcal. for the heat of sublimation of carbon. They also report on a variety of dissociation processes in these gases. Szwarc (113) discussed the thermal stability and reactivity of some hydrocarbon radicals. The bond dissociation energies of the latter were calculated and the variation in their magnitude related to their structure. He

(114) also presented tables of heats of formation and ionization potentials of hydrocarbon radicals.

THE AMERICAN CHEMICAL SOCIETY SYMPOSIUM

The definition of bond energies of Szwarc & Evans (116) was discussed by Glockler (53) who suggests the introduction of special influence factors in the definition in order to describe the effect of the molecular environment on the bond energy. A theoretical quantum mechanical paper by Mulliken (82) dealt with the structure of bond energies. He improved his magic formula (81) for the dissociation energy of molecules and, using three adjustable constants, he is now able to fit the CH-radical, nitrogen, oxygen, fluorine, methane, ethane, ethylene, and acetylene molecules with an average discrepancy of about ± 0.4 ev. Of especial significance is the insight gained of the factors affecting bond strengths. Pauling (89) reported on the formulation of an empirical equation which connects interatomic distances and bond number for multibond resonance. The sulfur-oxygen bond in sulfate ion has such type of resonance, involving one σ and two π bonds. Applying this equation it is found that in many complexes the amounts of multiple-bond character are such that all atoms become closely electroneutral. The methods of calculating bond lengths in large aromatic molecules were summarized by Coulson (22). Comparison of calculated and experimental values provides a complete vindication of the concept of fractional bond order. Chalvet & Daudel (14) show that there is for each bond-type a good relation between its exact Penney's bond order and the Pauling double bond character in the case of conjugated molecules. They also report on an empirical selfconsistent method for evaluating the bond orders and the atomic charges of a conjugated molecule, such as nitrogen tetroxide and in this case the large length of the nitrogen-nitrogen single bond finds an explanation. Szwarc (115) discussed the energetics of various types of dissociation processes and defined various terms such as bond dissociation energy etc. Differences in bond dissociation energies are compared with differences in heats of substitution. Special attention is given to processes where the same fragment dissociates from different molecules. Tentative values of resonance energies of radicals are obtained from bond dissociation energies.

The spectra and dissociation energies of the diatomic interhalogen molecules were dealt with by Durie & Gaydon (31). The emission band systems of bromine fluoride and iodine fluoride were analyzed and $D(\text{BrF}) = 2.16 \pm 0.02$ and $D(\text{IF}) = 1.98 \pm 0.04$ ev were reported. The dissociation energies and force constants of all the diatomic halogens and interhalogens were compared. Sutton (108) finds an inverse relation between bond lengths and dissociation energy for the carbon-chlorine bond in methyl and acetyl halides, and an inverse relation between the mean bond energy and the square of the bond length. Such relations indicate that the characteristics of the transition state are to some extent shown by the unperturbed state. Since it is unlikely that such a simple state of affairs will hold widely, more compounds must be examined.

The structure and microwave spectra of ethylene oxide, sulfide and imine and dichloromethane were investigated by Gwinn *et al.* (56). The potential barriers restricting inversion in ammonia, phosphine, and arsine were calculated by Costain & Sutherland (17) from their vibrational force constants to be 2070, 6000, and 11,200 cm^{-1} , respectively. For ammonia the calculated barrier differs only by 2 per cent from the value derived from inversion splitting in the spectrum by the Manning potential function. The barriers in phosphine and arsine would produce a splitting of only 10^{-5} cm^{-1} .

Mizushima, Morino & Shimanouchi (80) reported on problems of internal rotation based on their studies of the infrared and Raman spectra and their dipole moment and electron diffraction measurements on many molecules. They discussed their conclusions regarding the nature of the hindering potential on the basis of a steric force between atoms contained in different movable groups of the molecule. Riethof & Edgell (95) made some calculations of the vibration frequencies of molecules with many atoms and little symmetry. They use approximate normal co-ordinates, by two basically similar methods. The first method, which takes advantage of the existence of group frequencies has not yet been tested. The second method, dealing with molecules which are regarded to be simple derivatives of symmetrical molecules, has been tested with encouraging results. The contribution of neighbor interactions to paraffin properties was the subject of a report by Platt (94). Some of the quasi-additive properties such as heat of formation, molar refraction, molar volume, and boiling point differ among the various isomers of a given paraffin. The author gives a critical review of the various formulae found in the literature for calculating these differences. Torkington (126) has studied the theoretical problem of the possible motions of a system of vibrating particles. The case of the symmetrical vibrations of the symmetrical triatomic molecule such as water, sulfur dioxide, and chlorine monoxide was treated in detail. The infrared spectrum of hydrogen peroxide was re-examined and that of deuterium peroxide was obtained for the first time by Giguere & Bain (46). The observed frequencies were combined with the Raman spectra to calculate the force constants of the bonds. The results seem to support the lower value ($\sim 35 \text{ kcal.}$) for the bond energy of the oxygen-oxygen bond.

Bauer (3) reviewed the structure of a variety of volatile fluorides. He also reported new electron diffraction work on some of them and drew particular attention to those compounds where conflicting conclusions had been reached by electron diffraction and spectroscopic studies. The description usually given of the bond types of the M-F linkages is in terms of high electronegativity, ionic character, and multiple resonance. When these features are used simultaneously to describe the unexpected aspects of a bond, it only amounts to a formal restatement of the observed facts. It seems that insufficient attention has been given to the hybridization of the atomic orbitals used to represent the molecular orbitals of these molecules. Bernstein (5) derived relations between the additive physical properties of molecules in homologous series on the basis of a model in which strict additivity is assumed for the

contributions from nonbonded and bonded atoms. Relations are derived between bond energy and bond distance in homologous series in the case where the contributions from the bonded atoms are supposed to be nonadditive. The Raman effect of the germanium-hydrogen bond in germanium haloform molecules was studied by Delwaulle (27). The Raman spectra of the halogenated molecules of the fourth group elements were used to study the exchange of halogens between various molecules of this type. For example, chlorobromides and chloroiodides of carbon and silicon are stable. In the case of titanium, germanium and tin equilibria are established when AX_4 AY_4 molecules are mixed. An experimental investigation of the heat of dissociation of fluorine was presented by Wicke (137). He measured the heat conductivity of the gas and reports that $D(F_2) > 45$ kcal. A semiempirical relation between dissociation energy, vibration frequency and internuclear distance for diatomic molecules, indicates $D(F_2) \leq 50$ kcal. Preliminary experiments on the explosion method did not yet yield results.

Turning now to the general literature it must be said that the problems which beset the establishment of a system of bond energy values have not been solved. No agreement exists even on the definition of the term "bond energy" and several important quantities needed in the determination of numerical bond energy values, such as the heats of dissociation of nitrogen and fluorine and the heat of sublimation of carbon are still in question. It will be of interest to review the latest work on these three topics briefly. Since this review of the field is the first one to appear in these pages, it seems advisable to go into some detail concerning the concepts of bond energy, bond dissociation energy, and resonance energy as far as space permits. No experimental investigations of bond lengths by the x-ray and electron diffraction methods are included in this report.

THE HEAT OF SUBLIMATION OF CARBON

There are now known three experimental determinations of the heat of sublimation of carbon indicating $L(C) = 170.0$ kcal. (8, 78, 103) obtained from vapor pressure measurements at high temperature. The use of an accommodation coefficient of unity is questioned. A value of 125.0 kcal. is derived from spectrographic studies of predissociations in carbon monoxide by Herzberg (61). However, a different interpretation of the same data leads Gaydon (43) to propose $L(C) = 170$ kcal. Hagstrum (57) studied electron impact phenomena in carbon monoxide and arrives at $L(C) = 137.5$ kcal., while McDowell & Warren (79) deduce $L(C) = 120$ kcal. from similar impact work on methane and methyl cyanide. Field (40) considers electron impact data and contends $L(C) = 135$ kcal. as the best value from such experiments.

Kistiakowsky, Knight & Malin (69) mention indirect evidence favoring $L(C) = 170$ kcal. Glockler (49) suggests the higher value based on $D(CO) = 255.8$ kcal., using an argument concerning the similarity of properties of nitrogen and carbon monoxide. Pauling & Sheehan (90) proposed some novel ideas in a study of the dissociation of molecules. They define the hypothetical valence state of an atom as the isolated atom with the same electronic struc-

ture that it has in the molecule. The valence state of the atom is presumed to be the same in different molecules. They use a Birge-Sponer extrapolation of the vibrational levels to obtain the dissociation energy of the molecules into atoms in their valency states. This energy for oxygen is 0.74 and for carbon 1.73 ev. Subtracting their sum from the heats of dissociation of carbon monoxide in various electronic states yields such values as to indicate $L(C) = 140$ kcal. An excellent summary of the $L(C)$ problem has been written by Springall (105).

THE HEAT OF DISSOCIATION OF NITROGEN

For the calculations of bond energies of molecules containing nitrogen atoms, the heat of dissociation of nitrogen $D(N_2)$ must be known. However a controversy exists and three different values are available. Herzberg (61) and Douglas & Herzberg (29) favor 170 kcal. from a study of a predissociation in the upper state of the Lyman-Birge-Hopfield bands, where a clear breaking-off of the fine structure occurs at $v' = 6$, $J' = 13$, both in the P and Q branches. Hagstrum (57) arrives at $D(N_2) = 170.0$ kcal. from electron impact experiments. However Gaydon (43) presents arguments for $D(N_2) = 225.2$ kcal. and Glockler (50) considers 272.1 kcal. as a possible value by comparing carbon monoxide and nitrogen molecules. Besides $D(N_2) = 272.1$ and $L(C) = 170.0$ kcal. yield bond energy-bond distance curves for carbon-carbon, carbon-nitrogen, carbon-oxygen, nitrogen-oxygen, nitrogen-nitrogen, and oxygen-oxygen bonds which are similar to force constant-distance curves of the same bonds (51). Kistiakowsky, Knight & Malin (69) have studied detonation velocities in mixtures of gases containing cyanogen, oxygen and nitrogen and their results indicate that $D(N_2) = 170$ kcal. is too low. They cannot decide between 225.2 and 272.1 kcal., although they favor 225.2 kcal. because Herzberg (62) has adduced such strong evidence against the higher value. Hagstrum (57) deduced $D(N_2) = 170$ kcal. from appearance potentials. Brewer, Templeton & Jenkins (9) determined the heat of formation of cyanogen radical to be 94 ± 6 kcal., leading to the heat of dissociation of cyanogen into two cyanogen radicals of 114 ± 12 kcal. This new information does not allow any deduction concerning $D(N_2)$ because of the uncertainty in $D(CN)$. Pauling & Sheehan (90) support the low value $D(N_2) = 170$ kcal. with their valency state considerations of atoms. Branscomb (7) measured 31 bands, including the zero-zero band at $10,440 \text{ \AA}$ of the nitrogen first positive system in the afterglow of nitrogen. There is no evidence that the $v = 0$ level of the $B^3\Pi$ state is preferentially populated as required by the resonance theory of atomic reassociation using $D(N_2) = 170$ kcal. These experiments do not contradict this value for the recombination product may be the metastable $A^3\Sigma$ state. No clear-cut decision can be made at present regarding this important quantity, the heat of dissociation of nitrogen.

THE HEAT OF DISSOCIATION OF FLUORINE

The values deduced by earlier investigators for the heat of dissociation of fluorine $D(F_2)$ have been summarized by Glockler (48) and it appeared that

$D(F_2) \approx 60$ kcal. However, later work seems to indicate that this value should be lower. Schmitz & Schumacher (99) redetermined the ordinary heat of formation (Q_f) of chlorine monofluoride as 15.0 kcal., and since Wahrhaftig (131) had studied the absorption spectrum and deduced $D(ClF) \approx 60$ kcal. it appeared that $D(F_2) \approx 32$ kcal. Wicke (136) found $Q_f(ClF) = 21$ kcal. Eucken & Wicke (33) concluded from all available data that $D(F_2) = 40$ kcal., while Caunt & Barrow (13) determined the heat of solution of thallous fluoride (TlF to $TlF \cdot 800$ aq) to be 0.5 ± 0.2 kcal. exothermic. With other thermochemical data they derived an upper approximate limit of $D(F_2) = 45$ kcal. The existing data on the thermochemistry and spectrum of chlorine monofluoride were reviewed by Evans, Warhurst & Whittle (38). They decided in favor of the lower value $D(F_2) = 37 \pm 8$ kcal. This value was discussed in relation to the thermal dissociation of fluorine, the bond dissociation energies of the halogens and of structures isoelectronic with fluorine, the electron affinity of fluorine in solution, and the ionic character of covalent bonds involving fluorine atoms. Schumacher (100) from some thermochemical data got $D(F_2) = 30 \pm 8$ kcal. and Schumacher, Schmitz & Brodersen (101) found $D(ClF) = 60.2$ kcal. in the ground state and $D(ClF^*) = 8.3$ kcal. in the excited state. The absorption spectrum of hydrogen fluoride gas, examined by Safray, Romand & Vodar (98) has a long wave length limit leading to $D(HF) = 6.1 \pm 0.3$ ev agreeing with Gaydon (43). It corresponds to $D(F_2) = 51$ kcal. Andrychuk (2) studied the Raman spectrum of fluorine and found $\Delta G_{\frac{1}{2}} = 891.55$ cm^{-1} . Nathans (85) measured the absorption of fluorine in the infrared, but could draw no conclusion regarding $D(F_2)$. The classical method of equilibrium pressure measurement was applied by Doescher (28). His results indicate $D(F_2) = 38.9$ kcal. at 1000°K . A wave mechanical calculation by Johnston (68) leads to the extremely low value of $D(F_2) = 18 \pm 12$ kcal. via the calculated electron affinity. It is interesting to recall that Eyring & Kassel (39) were able to maintain a hydrogen-fluorine gas mixture at room temperature for some time without reaction occurring. This behavior would indicate that the heat of dissociation of fluorine is rather larger than the lower values proposed lately. Until the heat of dissociation of fluorine is known accurately, no bond energies of molecules containing fluorine atoms can be calculated.

BOND ENERGIES

Considering the difficulties with $L(C)$, $D(N_2)$, and $D(F_2)$, it is clear that definite values of bond energies for most important compounds cannot be given at this time. The situation is however still more complicated since the very definition of the term "bond energy" is still under discussion. Szwarc & Evans (116) and Evans (34) have made a very careful analysis of the concepts involved. First of all they distinguish clearly between "average bond energy" (B_i) and "bond dissociation energy" (D_i). The latter quantity is the energy needed to break a bond in the molecule. It is not necessarily equal to the bond energy of the bond in question. The latter is a certain portion of the total energy of atomization of the molecule ascribed to the

bond as it exists in the molecule. The question is how to divide the heat of atomization (Q_a) among the various bonds. The sum of all the bond energies (B_i) must equal Q_a . Similarly the sum of the successive D_i 's must also equal Q_a . There is no difficulty for a molecule which possesses only one kind of bond: for example $B(\text{CH in CH}_4) = 1/4 Q_a(\text{CH}_4)$. In ethane, $Q_a(\text{C}_2\text{H}_6)$ must be divided appropriately into portions representing $B(\text{C—C in C}_2\text{H}_6)$ and six $B(\text{CH in C}_2\text{H}_6)$. To carry out this apportionment in general it is necessary to have recourse to some other measurable bond property such as bond lengths and to make comparisons with other molecules of similar constitution. This procedure is no more arbitrary than similar considerations that have been made for any other additive property taking account of individual differences.

Szwarc & Evans proceed by defining the total energy (E) of the m -atomic molecule in terms of the n bond distances (r_k) and $3m-6-n$ angles (α_i), whence

$$E = f(r_1 \cdots r_n, \alpha_1 \cdots \alpha_{3m-6-n}) \quad 1.$$

or

$$dE = \sum_1^n \frac{\partial E}{\partial r_k} dr_k + \sum_1^{3m-6-n} \frac{\partial E}{\partial \alpha_i} d\alpha_i. \quad 2.$$

The integration of the right side of equation 2 depends on the path of integration and an infinite number of such paths are possible. For one such path L , the angles α_i are supposedly constant while the bond lengths are increased to infinity in such a way that $r_k = \gamma \cdot r_{k_0}$ ($1 < \gamma < \infty$). The k th integral is defined as the bond energy (q_k) of the k th bond. The sum of the q 's equals Q_a . If two bonds (k and j) are exactly alike, their q 's are alike. If a molecule contains n -like bonds, then $Q_a = nq$. These properties are the ones expected from bond energies.

The q 's so defined contain all of the interactions with the molecular environment. It seems desirable to make the definition of bond energy more detailed by using another set of parameters such that the influence of other nonbonded atoms or neighboring bonds is expressed explicitly. There are three possible assumptions that can be made, to describe these nonbonded interactions: (a) A Van der Waals type of interplay exists between the nonbonded atoms, as used in the central force field description of the molecule. In the triatomic molecule A—B—C , atoms A and C may interact in this manner. (b) The non-valence behavior is due to the influence of atom C on the bond AB, in the triatomic molecule A—B—C . Similarly atom A has an effect on bond BC. (c) Bond AB interacts with bond BC and vice versa. Such near-atom or near-group effects have been mentioned by several authors (4, 47, 93, 125).

The problem of the detailed nature of these influences on a bond caused by its environment is most important, but it need not be answered for the present purpose. It may be of the nature discussed by Heath & Linnett (60) for the water molecule caused by a change in hybridization of the oxygen-hydrogen bond caused by the presence of the other hydrogen atom. In gen-

eral it is a question of hyperconjugation as proposed by Mulliken, Rieke & Brown (84), and all features of interaction such as Van der Waals' and London dispersion forces. These fundamental concepts have been discussed by Pauling (88). Walsh (132) mentions five factors affecting bond energies. Coulson (20) remarks:

In the diatomic molecule the discussion of the bond even if hybridized orbitals are used cannot be carried out in the manner of covalent-ionic resonance but must take explicit account of the other non-bonding electrons.

And again (21):

Purely geometric considerations such as the number and relative positions of nearby atoms play a dominant part in determining bond lengths as is implied in a paper by Daudel, Sandorfy, Vroelant, Yvan & Chalvet (26).

The usual apparatus of discussing the chemical bond in terms of hybridization of orbitals, covalent-ionic resonance and possible double bond character must be amplified. The molecular environment of a given bond all depends on the distribution of the charge of the electron cloud in the molecule. The ultimate description must be rendered in terms of an improved mathematical apparatus of quantum chemistry.

In the meantime it is necessary to proceed empirically with the definition of bond energy. The second method mentioned above was studied by Glockler (53). This definition involves the heat of dissociation of the corresponding free radical of the bond in question and a reorganization energy (73) which describes two aspects: (a) The change in bond length from the bond as existing in the molecule to the free radical, and (b) certain terms which refer to the influences other atoms of the molecule have on a given bond.

In a molecule of m atoms each of the n bonds is affected by $m-2$ influence factors. The total number of the latter in the molecule is therefore $n(m-2)$. Since there are n bonds, it will be necessary to use $n(m-1)$ coordinates to describe the total energy of the molecule. Of these the number n refers to distances between bonded atoms (R) and f of them will describe interaction distances (r) between the bonds and the neighboring atoms influencing them:

$$E = f(R_1 \dots R_n, r_1 \dots r_f). \quad 3.$$

The bond energies (B) are expressed in terms of pure bond energies (B_0) which refer to the hypothetical pure bond stretching not counting the influence factors (I). As a specific example, the triatomic molecule ABC may be described as follows:

$$E = [R(AB, 3), R(BC, 3), r(AB, C; 3), r(BC, A; 3)] \quad 4.$$

and

$$B(AB; 3, \infty) = B_0(AB; 3, \infty) + I(AB, C; 3, \infty)$$

or

$$= RE_0(AB; 3, 2) + D(AB; 2, \infty) + I(AB, C; 3, \infty) \quad 5.$$

or

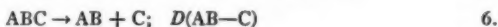
$$= RE(AB; 3, 2) + D(AB; 2, \infty)$$

and similar expressions for the bond BC. The numbers in parentheses refer to the limits of integration since these symbols are to be thought of as sums of increments of energy. This development can also be carried out on the basis of the near-bond effect. The only difference is that different numerical coefficients appear in the equations. The corresponding path of integration does not refer to a physically realizable one and there is no necessity that bond energies be defined in such a manner as to follow a physical path. The quantities here defined fulfill all the requirements of bond energies mentioned above. The problem of evaluating these influence factors has not been solved. Several investigations along the usual line concerning bond energies are described herewith.

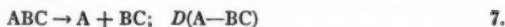
Tatevskii, Korobov & Mendzheritskii (124) and Tatevskii (122, 123) discuss the chemical structure of hydrocarbons, regularities in their heats of formation and their geometric configuration. The reason that additivity rules in the heats of formation of dienes, aromatic compounds, and in substances with conjugated unsaturated bonds do not hold is the neglect of the valence states of the carbon atoms comprising the structure. These authors estimate bond energies for these various valence conditions and the resulting calculated heats of formation are in excellent agreement with experimental values. Carbon-carbon bonds are classified into 12 groups, depending on the degree of unsaturation and carbon valence type. They give some general expressions for the heats of combustion involving the above ideas. Cook (16) presents calculations of bond energies of 12 homonuclear and eleven heteronuclear diatomic molecules and compares them with spectroscopic values. Tanaka, *et al.* (121) measured heats of combustion of some organo-silicon compounds. The heats of formation of the gaseous monatomic elements used were Si(85.0), O(59.1), H(51.7) and C(124.7) kcal. and the bond energies adopted were CH(87.3), C—Si(57.6), Si—O(89.3) and C—O(70.0) kcal. The resonance of the benzene ring was taken to be 39 kcal. Humphrey & Spitzer (67) determined the heats of combustion of *cyclo*-propane, -butane and -pentane, spiro-pentane, and methyl-*cyclo*-butane and checked their experimental results by calculations based on $B(CC) = 59$ and $B(CH) = 87$ kcal. A similar investigation on the heats of combustion of a number of nitrogen containing compounds was undertaken by Cole & Gilbert (15). They attempted to evaluate the nitrogen-nitrogen and nitrogen-hydrogen bond dissociation energies based on $D(N_2) = 225.2$ kcal. They found $D(N-N$ in hydrazine) = 60; $D(N-N$ in phenylhydrazine) = 48; $D(N-N$ in hydrazobenzene) = 38 and $D(N-N$ in tetraphenylhydrazine) = 31 kcal. The $N=N$ bond is stronger: $D(N=N$ in transazobenzene) = 105 and $D(N=N$ in cisazobenzene) = 93.4 kcal.

BOND DISSOCIATION ENERGY

This quantity refers to the physically realizable process of breaking a bond in a molecule. Szwarc & Evans (116) emphasize its significance. In the triatomic molecule A—B—C it is the energy $D(AB-C)$ for the reaction of removing the atom C from the molecule



or $D(\text{A}-\text{BC})$ for the reaction



where now equation 2 is integrated along the physically realizable paths P and P' and the quantities $D(\text{AB}-\text{C})$ and $D(\text{A}-\text{BC})$ can actually be measured. Comparing them with the bond energies of bonds AB and BC it is seen that the difference lies in the paths of integrations P and P' as compared with L . Another important quantity, the reorganization energy of a bond is involved in these considerations. It was first discussed by Long & Norrish (73). Adding to $D(\text{AB}-\text{C})$, the heat of dissociation $D(\text{AB})$ of the free radical must yield the heat of atomization ${}_3Q_a$. Similarly $D(\text{A}-\text{BC}) + D(\text{BC}) = {}_3Q_a$.

Still considering the triatomic molecule $\text{A}-\text{B}-\text{C}$, the bond dissociation energy as written in terms of Glockler's (53) notation, involving the molecular environment explicitly, via the I factors, is

$$\begin{aligned} D(\text{AB}-\text{C}) &= RE_0(\text{AB}; 3, 2) + I(\text{AB}, \text{C}; 3, \infty) \\ &\quad + RE_0(\text{BC}; 3, 2) + D(\text{BC}; 2, \infty) + I(\text{BC}, \text{A}; 3, \infty) \quad 8. \\ &= RE(\text{AB}; 3, 2) + D(\text{BC}; 2, \infty) + RE(\text{BC}; 3, 2) \end{aligned}$$

and similarly

$$D(\text{A}-\text{BC}) = RE(\text{AB}; 3, 2) + D(\text{AB}; 2, \infty) + RE(\text{BC}; 3, 2). \quad 9.$$

The difference of these two dissociation energies is $D(\text{BC}; 2, \infty) - D(\text{AB}; 2, \infty)$ as expected. The dissociation paths just described are artificial in the sense that the energies $D(\text{AB}-\text{C})$ or $D(\text{A}-\text{BC})$ cannot be supplied to the molecule one term at a time as expressed on the right side of these equations. It is not possible to cause the reorganization of the bond AB, i.e., supplying the necessary energy $RE(\text{AB}; 3, 2)$ only. The energy represented by all three terms must be added to the molecule simultaneously in order to cause the corresponding dissociation of the bond. These paths of integration lead to the same result as do the path P and P' of Szwarc & Evans (116).

These studies of the definition of bond energies should lead to a clearer understanding of these quantities. In numerical application it will be necessary to neglect some of the influences of atoms far removed from a given bond. Some attempts along these lines have already been made in the case of branched paraffins (47).

Szwarc (110) has written an excellent review on the subject of the determination of bond dissociation energies by pyrolytic methods, which covers the field through the year 1949. In a supplement (112) he reviews the processes which lead to a determination of bond dissociation energies: (a) The process of formation of a bond by the association of the respective radicals or atoms, and (b) the process of fission of a bond resulting in the formation of the respective radicals or atoms. The first method is very difficult to carry out experimentally. The bond breaking method may be divided into three groups: (a) The photochemical method, where the energy is applied by radiation; (b) the electron impact method where the kinetic energy of an electron beam is used, and (c) when the bond splitting energy is thermal energy.

Especially interesting are the results obtained using toluene as a carrier gas. All the conditions and restrictions which have to be watched in carrying out these pyrolysis experiments are discussed clearly. The effects of various constitutional factors on the bond dissociation energies are mentioned.

A number of workers have determined a variety of bond dissociation energies: the pyrolysis of butene-1 yields allyl and methyl radicals. The bond dissociation energy $D(\text{H}_2\text{C}:\text{CH}\cdot\text{CH}_2-\text{CH}_3) = 61.5$ kcal., giving $D(\text{H}_2\text{C}:\text{CH}\cdot\text{CH}_2-\text{H}) = 76.5$ kcal. and the heat of formation $Q(\text{H}_2\text{C}:\text{CH}\cdot\text{CH}_2\cdot) = 30$ kcal., according to Sehon & Szwarc (102). The latter author (113) finds that the bond dissociation energies of radicals are lower than the ones for the parent hydrocarbon: $D(\cdot\text{H}_2\text{C}\cdot\text{CH}_2-\text{H}) = 38$; $D[\cdot\text{H}_2\text{C}(\text{CH}_3):\text{CH}-\text{H}] = 39$; $D[\cdot\text{H}_3\text{C}(\text{C}_2\text{H}_5):\text{CH}-\text{H}] = 40$; $D(\cdot\text{H}_2\text{C}\cdot\text{CH}_2-\text{CH}_3) = 25$; $D(\cdot\text{H}_2\text{C}\cdot\text{CH}_2-\text{C}_2\text{H}_5) = 26$; $D[\cdot\text{H}_2\text{C}(\text{CH}_3):\text{C}-\text{H}] = 68$ and $D[\cdot\text{H}_2\text{C}(\text{CH}_3):\text{C}-\text{CH}_3] = 57$ kcal. Szwarc, Ghosh & Sehon (117) determined the carbon-bromine bond dissociation energies in benzyl and allyl bromides to be $D(\phi\cdot\text{CH}_2-\text{Br}) = 50.5$ and $D(\text{CH}_2:\text{CH}\cdot\text{CH}_2-\text{Br}) = 47.5$ kcal. The influence of aromatic substitution on the carbon-bromine bond dissociation energy is rather small according to Szwarc, Leigh & Sehon (118); *o*-, *m*-, *p*-chloro, *m*-, *p*-bromo, *o*-, *m*-, *p*-methyl, *m*-, *p*-nitro and *m*-, *p*-nitrile substituted benzyl bromides were studied. The differences $\Delta D = D(\phi\cdot\text{CH}_2-\text{Br}) - D(\phi_s\cdot\text{CH}_2-\text{Br})$ range from 0 to 2 kcal. They were obtained from the expression $\Delta D = 2.3 RT \log (k_s/k_u)$ where the subscript "s" refers to the substituted benzyl bromide. Szwarc & Sehon (119) measured the rate of pyrolysis of trichlorobromomethane and found $D(\text{Cl}_3\text{C}-\text{Br}) = 48$ kcal. The rate is unimolecular. They point out the great difference between $D(\text{H}_3\text{C}-\text{Br}) \approx 68$ and $D(\text{Cl}_3\text{C}-\text{Br}) = 48$ kcal. and they attribute this difference mainly to steric repulsion between the bulky chlorine and bromine atoms in the trichlorobromomethane molecule, since some preliminary studies on trifluorobromomethane indicate that $D(\text{H}_3\text{CBr}) - D(\text{F}_3\text{CBr}) \approx 4$ kcal. The effect of halogenation on the carbon-bromine bond dissociation energy in halogenated methanes was further studied by the same authors (120). Since the rate constants were affected by the toluene pressure (except in the case of trichlorobromomethane and carbontetrabromide), they did not calculate the activation energies from the temperature coefficient of the respective rate constants. The bond energies were obtained from the rate constant of unimolecular decomposition, $k = \nu \cdot \exp(-D/RT)$ assuming the frequency factor (ν) to be constant for the whole series (2×10^{13} sec.⁻¹) obtained from methyl bromide [$D(\text{H}_3\text{C}-\text{Br}) = 67.5$ kcal.]. The results are: $D(\text{F}_3\text{C}-\text{Br}) = 64.5$; $D(\text{H}_2\text{ClC}-\text{Br}) = 61$; $D(\text{HCl}_2\text{C}-\text{Br}) = 53.5$; $D(\text{Cl}_3\text{C}-\text{Br}) = 49$; $D(\text{H}_2\text{BrC}-\text{Br}) = 62.5$; $D(\text{HBr}_2\text{C}-\text{Br}) = 55.5$ and $D(\text{Br}_3\text{C}-\text{Br}) = 49$ kcal. The striking feature is the decrease in $D(\text{X}_3\text{C}-\text{Br})$ in the series CH_3Br to CX_3Br . The explanation is sought in the steric repulsions of the halogen atoms, which increases with the number of chlorine and bromine atoms in the molecule. Evans & Szwarc (37) made an interesting calculation of the ionization potential of allyl radical $I(\text{H}_2\text{C}:\text{CH}\cdot\text{CH}_2\cdot) = 9.05$ ev using a combination of appropriate appearance potentials and bond dissociation energies. From a study of the photochemical and thermal

decomposition of neopentane, Hormats & Van Artsdalen (64) deduced values of $D(C_5H_{11}-H) = 94$ and $D(C_4H_9-CH_3) = 79$ kcal. Hartley, Pritchard & Skinner (58) report the dissociation energies of the two methyl-mercury bonds in mercury dimethyl to add up to 57.4 ± 4 kcal. The removal of the first methyl group required 51 kcal., and of the second one, 6 kcal. The carbon-mercury bonds in the methyl-mercuric halides have the following dissociation energies: $D(H_3C-HgCl) = 63.4 \pm 2.5$; $D(H_3C-HgBr) = 60.7 \pm 2.6$ and $D(H_3C-HgI) = 59.0 \pm 3.3$ kcal. The same authors (59) studied the thermochemistry of other mercury alkyls and found that the fission of both ethyl groups from mercury-diethyl needs 45.1 ± 6 kcal. and it appears that the removal of the first ethyl group requires 40 kcal. The dissociation energies of the ethyl-mercury halides are as follows: $D(C_2H_5-C_2H_5) = 58.0 \pm 3.8$, $D(BrHg-C_2H_5) = 55.5 \pm 4.5$ and $D(IHg-C_2H_5) = 54.2 \pm 5.6$ kcal. Cottrell & Reid (18) and Hillenbrand & Kilpatrick (63) have studied the thermal decomposition of nitromethane. The rate determining step is the breaking of the carbon-nitrogen bond and $D(H_3C-NO_2) = 52$ kcal.

Several mass spectroscopic investigations have yielded certain bond breaking energies. Stevenson (106) studied cyanogen, hydrogen cyanide, and cyanogen chloride by electron impact and deduced $D(NC-CN) = 6.90$ or 4.64 ev depending on the state of the cyanogen radical. The bond dissociation energies of CH_3 , CH_2 , and CH radicals were obtained by McDowell & Warren (79). Using $D(CH_3-H) = 4.43$ ev, $D(CH_2-H) \leq 3.45$, $D(CH-H) \leq 3.40$ and $D(CH) \leq 3.6$ ev indicates that $L(C) = 120$ kcal. Geerk & Neuert (44) measured appearance potentials in methane, methyl alcohol, and methylal. In general their results agree with earlier work.

Several authors made more or less empirical calculations of bond dissociation energies. Assuming that the overlap integral between two carbon atoms gives a measure of the bond dissociation energy of a hybrid bond involving carbon, Maccoll (76) finds that the bond dissociation energy of hybrid bonds increases $sp > sp^2 > sp^3$. Bryant (12) calculated free energies of formation of *iso*-propyl, *tert*.-butyl, vinyl, phenyl, and the first twelve *n*-alkyl gaseous free radicals from bond dissociation energies and values derived from molecular entropies. Empirical equations for the carbon-hydrogen and carbon-carbon bond dissociation energies in saturated hydrocarbons and free radicals were given by Voevodskii (129).

New information in the inorganic field is rather limited. Trotman-Dickenson & Steacie (127) obtained the activation energy of the reaction between methyl radicals and ammonia and thereby determined an upper limit for the dissociation of ammonia: $D(H_2N-H) = 112$ kcal. if the usual value $D(H_3C-H) = 102$ kcal. is accepted. Edse (32) gives $D(HO-OH) = 46.3$ kcal. The dissociation energies of calcium and magnesium oxides are 5.2 ev according to Huldt & Lagerquist (66) who used the flame method. Gilles (45) determined the dissociation energy of the oxygen-chlorine bond in $HOX(X = I, Br, Cl)$ to be 56, 56, 60 kcal., respectively. The binding energy of a number of gaseous alkali halides were calculated on a semiempirical classical basis by Rittner (96).

RESONANCE ENERGY

There are several ways of defining resonance energies. When reference is made to some preconceived structure of the molecule (91) then a knowledge of bond energies is necessary. It is important to realize that some of the usual methods of calculating resonance energies involve all the strengthening and weakening effects which bonds may suffer in a given molecular environment.

For example, the resonance energy of butadiene is usually given as 3.5 kcal. (135) based on the heats of hydrogenation of butene (30.3 kcal.) and butadiene (57.1 kcal.). Ordinarily twice the former minus the latter of these values is called the resonance energy of butadiene. However, Glockler (52) showed that this view is based on the assumption that butene and butane have ethylene-ethane-like bonds. On this basis the difference of the actual atomic heat of formation and the same quantity for the reference structure is 19.0 kcal. If butadiene were referred to butene, its resonance energy is 13.4 kcal.

In order to avoid the difficulties in the determination of resonance energies from bond energies Szwarc (111) proposes to use experimental bond dissociation energies as a basis for defining "experimental resonance energies." The idea is expressed in the following example, using methane and ethane

$$[RS(CH_4) - RS(C_2H_6)] - [RS(CH_3\cdot) - RS(C_2H_5\cdot)] = D(CH_3-H) - D(C_2H_5-H)$$

$RS(C_2H_5\cdot)$ equals the difference on the right side only if the first bracket and also $RS(CH_3\cdot)$ are zero. On this view he finds for example $RS(\phi\cdot CH_2\cdot) = D(CH_3-H) - D(\phi\cdot CH_2-H) = 101.0 - 77.5 = 23.5$ kcal. He says that it is impossible to disentangle in an absolute way the factors which influence molecules such as steric considerations, the ionic character of bonds and other strengthening and weakening effects. He calculates the strengthening effect in a series of normal paraffins (C_3-C_{10}) for the individual bonds. These considerations are mainly exploratory and tentative. The real purpose of the analysis is to stress the difficulties encountered when molecular energetics are treated on the bond energy basis. It does not seem possible to treat resonance energies of molecules by this approach.

It is shown by Duchesne (30) that hybridization of end-atoms in multiple bond molecules, as well as in single bonded ones, is necessary for the understanding of chemical bond properties. Resonance effects seem to play a minor role except for conjugated systems. The use of group equivalents for the calculation of resonance energies was studied by Franklin (41) using heats or free energies of formation. These values are compared with resonance energies derived from bond energies, heats of combustion, and hydrogenation energies, with good agreement. Hornig (65) attempted to evaluate the factors such as bond compression and also the basis of calculating the resonance of benzene. The resonance energy of cyclobutadiene was found to be 15 kcal. by Van Dranen & Ketelaar (128) based on theoretical calculations of valence bond parameters. Parr (87) used the linear combination of atomic orbitals (LCAO) method to determine theoretical resonance energies. He finds $RS(C_6H_6) = 73.1$ kcal. and $RS(\text{trans-1,3-butadiene}) = 6.5$ kcal.

In a very interesting paper Mulliken & Parr (83) use the LCAO molecular orbital method to compute resonance energies for benzene and butadiene and they give a general analysis of the theoretical versus the thermochemical approach. The gross (vertical) resonance energy is 73.1 kcal. for benzene taken at $R(\text{CC}) = 1.39 \text{ \AA}$. In order to compare it with the usual empirical value they calculate the compression energy from 1.39 to 1.54 or 1.33 \AA . Other corrections involve hyperconjugation and related effects. These corrections are estimated and the computed resonance energy is 36.5 kcal. The thermochemical value is 41.8 kcal. The gross resonance energies of *cis*- and *trans*-butadiene are 7.8 and 6.5 kcal. For *trans*-butadiene the calculated value corrected for compression is 3.7 kcal. (observed 6.5 kcal.). A new kind of bond energy is introduced by Brown (10) as the "bond localization energy." It is the energy required to perturb the molecule so that the bond becomes a double bond, i.e., two of the π electrons are localized in the bond. Its relation to the activation energy is indicated. It can be expressed in terms of resonance energies of certain molecules related to the given one. There is a close relation between mobile order and bond localization energy. Magnus & Becker (77) made precision measurements of combustion heats of some higher aromatic hydrocarbons and obtained a qualitative check between experimental and quantum mechanical values. An empirical method of estimating resonance energies was introduced by Brown (11). He defines a molecular orbital quantity called the "annulation energy," as the loss in resonance energy caused by the fusion of aromatic ring systems into a larger structure. It is simply related to the mobile bond orders of the two bonds undergoing fusion. Coulson & de Heer (23) and Evans & de Heer (36) used quantum theoretical calculations for the discussion of additivity relations for approximating resonance energies of hydroquinones and quinones. From appearance potential measurements Franklin & Lumpkin (42) find that the energy required to rupture similar bonds is the same whether or not the resulting carbonium ion is capable of resonance. They studied allyl, benzyl, cyclohexyl-dimethyl carbinyl, and phenyl-dimethyl carbinyl ions. Bhagwat & Shukla (6) think that resonance stabilization should cause a reduction in molar volume. The observed parachor should therefore be less than the calculated values. This effect is found in carbon dioxide, carbon suboxide, nitrous oxide, hydrazoic acid, carbon disulfide, and aliphatic diazo compounds.

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HETEROGENEOUS EQUILIBRIA AND PHASE DIAGRAMS¹

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The practical application of the monumental memoir of Gibbs to the elucidation of the equilibria in chemical systems was first suggested by Roozeboom (1). Among other applications he proposed the study of metallurgical systems and soon afterward published a remarkably complete phase diagram of the iron-carbon system. This initial work was intensively followed up by C. H. Desch and others. For many years the study of phase relationships in alloys has been a standard part of the training of every student of metallurgy. Beginning with the work of Van't Hoff and his co-workers on the Stassfurt salts, chemists have studied extensively the heterogeneous equilibria of systems in which the experimental difficulties are not formidable. The study of equilibria in solids other than metals, in liquid-solid high melting systems, and in systems requiring high-pressure techniques has lagged because of experimental difficulties. Included in these more difficult experimental areas are most mineralogical and ceramic systems. Since this review is limited in extent by editorial specification and since important advances are now being made in such systems, we have chosen to discuss these in this review.

MINERALOGICAL SYSTEMS

EXPERIMENTAL PROCEDURE

Experimental Technique. The techniques used in research on mineralogical systems vary widely with the nature of the materials involved. Laboratory synthesis by mere fusion in air or in a vacuum has been particularly effective in clarifying some of the complex metallic sulfide [Berry *et al.* (2); and Graham (3)] selenide [Earley (4)], and antimonide systems [Graham & Kaiman (5)]. Solid-state reactions by various sintering techniques are also common, and frequently they yield information relatively difficult to obtain otherwise. Thus Hatch *et al.* (6) found solid-state reactions to be the only method for the synthesis of fluorine-muscovite, and similarly Foster (7) was able to synthesize sapphirine ($4 \text{ MgO} \cdot 5 \text{ Al}_2\text{O}_3 \cdot 2 \text{ SiO}_2$) by this method. For most silicate systems, however, particularly where crystal-liquid equilibria are involved, the quenching technique is used.

Some of the oxide systems in particular require the use of very high temperatures, and developments in methods of obtaining, controlling, and measuring such temperatures have had to precede study of such systems. Temperatures over 2000°C. have been obtained in electrical furnaces making

¹ The survey of the literature pertaining to this review was concluded in December, 1951.

use of the high-temperature electrical conductivity of rods of the rare earth oxides, and Conn (8) has attained temperatures well over 3000°C. by the use of sunlight reflected from a large paraboloidal mirror. For most silicate work, where the quenching technique is used, temperatures are within the working range of platinum resistors (600° to 1600°C.); the major experimental problem is the accurate control and maintenance of these temperatures, for days or even for weeks. A discussion of the technique used at the Geophysical Laboratory of the Carnegie Institution in Washington, D. C., is given by Roedder (9), and Eubank (10) has described an electronic controller capable of maintaining temperatures up to $1550 \pm 0.1^{\circ}\text{C.}$ for several hours, or $\pm 1.0^{\circ}\text{C.}$ for several days. The special techniques used in high-pressure studies are discussed below.

Determination of Equilibrium Conditions. Experimental phase equilibrium studies involve two major problems: first, the establishment and proof of equilibrium, and second, the determination of the existence and composition of the phases present at equilibrium. In the first volume of this Review, Brewer (11) discussed a number of the methods used to verify equilibrium. Unfortunately, however, no method of experimental or theoretical determination of phase relationships in a heterogeneous system can completely exclude the possible existence of other, more stable phases. Metastable phase diagrams can appear perfectly normal in all respects, and unless the possibility of the existence of other modifications or compounds can be deduced from crystal chemical considerations or from the occurrence of such phases in other systems, the diagrams will appear to represent true equilibrium conditions. The existence of metastable equilibrium, even for long periods of time at high temperatures, is particularly common in the silicates and may be practically impossible to avoid. Thus in a part of the system $\text{K}_2\text{O}-\text{MgO}-\text{SiO}_2$ Roedder (9) was unable to establish equilibrium at the liquidus with the "correct" modification of silica (quartz), known from other systems to be the stable modification at such temperatures. Similarly, no evidence for the existence of the compound $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ was found in any of the experimental work on the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ [Schaerer & Bowen (12)], yet this compound exists in nature as the mineral jadeite. It is not known whether jadeite is the stable form under any of the conditions used in the experimental work, as all attempts to synthesize it have failed [Yoder (13)]. Several other natural minerals such as the garnets almandite ($3\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) and grossularite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$), and the pyroxene ferrosilite ($\text{FeO} \cdot \text{SiO}_2$) behave similarly. Other than the possibility of monotropism, these may be stable only under higher pressures, or at other temperatures, or they may possibly represent phases which are truly stable under some of the experimental conditions used. In this last case, presumably the reactions forming them have activation energies which are prohibitive of laboratory synthesis, but are permissive if geological time is available.

Identification of Phases. The identification of the phases present and the determination of their composition is sometimes one of the most difficult aspects of phase equilibrium studies. Any characteristic property of a phase

may be measured to prove its existence or to discern a phase change [Brewer (11)], and hence recent developments in instrumentation and a wider use of older techniques will do much to aid phase identification. Anderson *et al.* (14) had to use thermomagnetic analysis, along with x-ray and gravimetric analyses, to determine the exact nature of the carbon-bearing phase present in iron catalysts for the Fischer-Tropsch process. Similar thermomagnetic analyses were used by Kiskyras (15) to distinguish two modifications of ferrous sulfide found in nature, whose chemical compositions are remarkably close, and measurements have been made of the magnetic susceptibilities of natural chromites of varying composition [Peoples & Eaton (16)]. Infrared adsorption spectra have also been determined for a number of minerals and in certain cases are very helpful [Adler (17)].

If good crystals are available, the existence of very closely related polymorphs can sometimes be detected with accurate reflecting goniometer measurements of crystal interfacial angles, as in the discovery of natural crystals of three new polymorphs of zinc sulfide [Fron del & Palache (18)]. With x-ray study, these new types proved to be isotypic with several forms of silicon carbide [Ramsdell (19)], in that they represent different stacking sequences, all with identical composition and closely related structures, but with unit cells multiples of that of wurtzite. Wittels (20) used a novel high-temperature, dilatometric method to detect structural transformations in single crystals of the amphiboles, and Frueh (21) was able to detect a marked change in the electrical resistivity of the mineral bornite (Cu_5FeS_4) in the vicinity of the temperature of complete disorder forming the high-temperature disordered phase at 220°C . Narayanaswamy (22) found differences in the Raman spectra of high and low quartz (SiO_2) which may well open a new avenue for research on silicates.

Determination of the amount and composition of liquid present at high temperatures (or glass, its quenched equivalent) has been a considerable problem in many silicate systems, as glass does not have many of the properties so characteristic of crystalline solids. Centrifuging at high temperatures to separate liquid from crystals should work rather well, as an adaptation of the well-known "wet-rest" method used so frequently in soluble salt-water systems at lower temperatures [for example see Campbell *et al.* (23)], but experimentally this method presents serious problems at high temperatures. Heat-of-solution calorimetry has been used to determine the amount of liquid (glass) present in Portland cement clinker, in consequence of the differences in heat of solution of crystals and that of glass [Lerch & Brownmiller (24)], but this requires a knowledge of the latent heat of crystallization of all possible glass compositions in the system. The determination of the approximate amount of liquid present by the "quenching" technique is usually based on microscopical examination for glass in the quenched product. A more accurate method is available, however, when the index of refraction of the glass in the mixture of glass plus crystals can be obtained. If one knows the total composition of the mixture (by synthesis) and the composition of the crystal phase present (from petrographic examination), by use of a

previously determined plot of composition versus index of refraction for glasses in the system, one can determine both the composition of the glass and the relative amounts of crystals and glass present in the quenched sample. In silicate systems these determinations of amounts of liquid and crystal phases are usually used only as a guide to further work, and seldom as data on which to base an equilibrium diagram. For the determination of the temperature of eutectic points by observing the start of melting of all crystalline material, microscopic examination for the presence of glass is not so sensitive a test sometimes as is the sintering of the powdered crystalline material.

Although in general a combination of thermal, x-ray, and microscopic data is used to determine the composition and interrelationships of phases, the petrographic microscope is still the most useful tool in silicate studies, even when the optical properties of the phases are unknown at the start of the investigation [for example see Roedder (9)]. Petrographic methods are particularly useful with the quenching technique, as the quantity of sample required for a complete optical determination is very small. As many as seven distinct optical properties, any one or combination of which may be definitive of a phase, may, if necessary, be measured on a single crystal grain less than 10 microns in diameter without destroying the grain. It is far more convenient, however, to use different portions of the sample for each such determination, and hence 1 mg. or more of sample is desirable, and as most of the procedures used in the quenching technique provide samples of approximately 10 mg., there is adequate material left for other techniques such as the x-ray. Petrographic analyses are frequently used as a quantitative and accurate check on chemical analyses of complex mixtures such as rocks and meteorites [for example see Wahl (25)].

The use of x-ray techniques has progressed considerably in the last year. X-ray determination of the unit cell frequently helps to clarify problems of chemical composition or crystal morphology, as in the study of the compound schairerite [$\text{Na}_2\text{SO}_4 \cdot \text{Na}(\text{F}, \text{Cl})$] by Wolfe & Caras (26). X-ray techniques are not a panacea, however, and some of the limitations have been discussed by Brewer (11). Because of the minute percentage of crystalline phase present, such techniques are useless for determining the crystal phase at the liquidus unless such crystals can be identified by petrographic methods with other crystals occurring in larger amounts in samples equilibrated at lower temperatures. Of particular significance is the limitation of x-ray techniques in systems involving solid solution series between "end members" whose unit cells are practically identical, as is the case in the system MgAl_2O_4 — ZnAl_2O_4 [Kordes and Becker (27)]. Claisse (28) has used measurements of the separation between two adjacent x-ray powder pattern lines as a sensitive measure of composition in a solid solution series, thus eliminating various experimental errors inherent in absolute measures of Bragg angles or d/n values. Increasing use of x-ray structural analysis will certainly help to reconcile some of the contradictory data on many crystalline phases, as in the application of Fourier projections to prove the existence of a simple structure for the titanium-carbon-nitrogen compound occurring in blast furnace salamanders

[Weeks, McLachlan, and Lewis (29)]. X-ray powder pattern methods are also being applied to resolve the physical components in coals [for example see Siever (30)].

Of all the techniques for the identification and understanding of solid phases in mineral systems, differential thermal analysis (DTA) has seen perhaps the greatest increase in popularity in recent years. The use of cooling curves has been a standard practice in metallurgical phase investigations for many years, and in essence, DTA is a similar procedure, with two important differences. DTA studies on minerals usually involve only heating curves, and in most cases the thermal effects recorded do not represent reversible reactions such as melting and crystallization. Cooling curves are not effective in most silicate work as the heats of crystallization are low and crystallization may be exceedingly sluggish. Many mineral phases, however, include either the carbonate or hydroxyl ion as a specific part of the crystal structure. If these minerals are heated, there will usually be thermal effects attendant on driving off water or carbon dioxide, and frequently the resulting disorganized structure will recrystallize to a new phase at still higher temperatures, giving an additional thermal effect. Any rapid transition, such as α to β quartz will also show up, and if reversible, may be seen on cooling as well. As mineralogical DTA studies are usually done at temperatures up to only 1000°C., no melting is to be expected from most minerals or their decomposition products. The usual convention is to plot temperature differential, in arbitrary units, as the ordinate, and reference sample temperature as the abscissa. When DTA curves are unlabeled, it is usually safe to assume that exothermic reactions are shown as upward deviations from the base line.

A number of methods have been developed to make DTA more sensitive and significant for certain types of minerals by eliminating or controlling as well as possible many of the factors which may affect DTA curves. It has become increasingly apparent that the atmosphere in which the samples are heated may greatly influence the DTA curves obtained. Either a vacuum is maintained around the sample [Whitehead & Breger (31)], particularly in the studies of the substances present in coals and lignites [for example, Smothers & Chiang (32), and Whitehead & King (33)], or else a neutral or oxidizing atmosphere is used [Rowland & Lewis (34)].

The carbonate minerals are under intensive study by DTA methods, and the effects of solid solution on the DTA curves have been recorded by Faust (35) and by Kulp *et al.* (36). Rowland & Beck (37) have found that under some conditions the method can detect as little as 0.3 per cent dolomite in a rock, but Graf (38) has shown that the very small quantities of water-soluble salts frequently present in natural dolomites may seriously affect the size, shape, and position of the definitive endothermic peak for dolomite at 700°–800°C.

The apparatus used for DTA varies considerably with the nature and number of the specimens to be studied. A discussion of the method, theory, and apparatus is given in one of a series of reports on the identification and significance of the various clay minerals [Kerr, Kulp, & Hamilton (39)].

Smyth (40) has discussed the significance and interpretation of DTA curves and McConnell & Earley (41) have described an integrated DTA apparatus. Actually DTA can be used either as a relative method to compare specimens, or as a microcalorimeter, detecting heat effects on the order of 1 cal./gm. or less on samples weighing considerably less than 1 gm. [Wittels (42)], and many examples are found in the literature of the use of DTA in specific problems such as the nature of flint and chalcedony [Midgley (43)], the temperature of deposition of quartz [Tuttle, (44), Keith & Tuttle (45)], structural changes in the amphiboles [Wittels (20)], the compounds present in natural hydrated ferric hydroxides [Kulp & Trites (46)], and the age of metamict minerals [Kerr & Holland (47)].

ANHYDROUS SYSTEMS

Unary Systems. A review, up to 1948, of phase transformations in one-component silicate systems is given by Kracek (48), and the crystallographic aspects of such transformations are discussed by Buerger (49). Careful study of several minerals has revealed complexities which were not apparent at first sight. For example, millerite (NiS) occurs as two modifications, and the fact that β millerite does not occur in the natural mineral would indicate that millerites have formed below 396°C. in nature, neglecting corrections for pressure etc. [Gritsaenko *et al.* (50)]. The mineral pyrrhotite (essentially FeS) appears to be far more complicated than originally was thought [Kiskyras (15)], and the various polymorphs of the compound $\text{MgO} \cdot \text{SiO}_2$ have been the subject of study by high-temperature x-ray techniques to rationalize the relationships between the three or more crystalline modifications [Foster (51)]. Experimental and theoretical investigation of the graphite \leftrightarrow diamond equilibrium has been recorded by Bridgman (52) and by Leipunskii (53). It is fairly certain that the theoretically calculated line representing equilibrium between graphite and diamond has a positive slope on the pressure-temperature (PT) plot, and that diamond is not the stable phase at atmospheric pressure and temperature, but the shape of the line has been subject to two interpretations. By either interpretation, if graphite could be subjected to sufficiently high pressures, it could be made to transform into diamond, the rate, however, being exceedingly slow unless the temperature used is high, in which case still higher pressures are needed. [Eyring & Cagle (54)]. Bridgman (52) used pressures up to approximately 640,000 lb. per sq. in. at estimated temperatures over 2000°C. for seconds in an unsuccessful attempt to synthesize diamond from graphite. The experimental work would seem to indicate, however, that the field in which diamond is stable is not far from the conditions obtained, thus making the possibility of the synthesis of diamond for its many industrial applications appear less remote than heretofore.

Significant variations in the temperature of the reversible $\alpha \leftrightarrow \beta$ transformation at 573°C. in quartz, at atmospheric pressure, have been reported by Tuttle (44), and by Keith & Tuttle (45), using sensitive DTA methods. These variations, in what has sometimes been considered a good thermo-

metric reference point, amount to nearly two degrees in natural quartz samples from various occurrences, and are connected systematically with the geologic type of origin and hence with the conditions of temperature (or composition) prevalent during the crystal growth. Synthetic crystals of quartz grown in environments containing elements which might possibly substitute for Si^{+4} in the lattice (Ge^{+4} or the combination Li^+ and Al^{+3}) had individual transformation temperatures scattered over a range of nearly 200° , some falling above and some below that of the natural materials (personal communication, Tuttle). This would seem to indicate that differences in the permissible amounts of solid solution of these ions in the two forms of quartz may be a major controlling factor, but there are still unresolved irregularities in the thermal behavior of some samples. The influence of adsorbed gas on the α - β transformation of quartz has been studied by Stahl (45a). The transformation temperature decreases as the amount of adsorbed gas increases, varying from 572.0°C. to 578.0°C. This suggests that the transformation may be initiated at the surface of the crystal.

The temperature of the transformation of a single sample of quartz has been examined by Yoder (55) as a function of pressure, up to approximately 145,000 lb. per sq. in., and has been found to increase rather uniformly from 572.3°C. at atmospheric pressure to 815°C. at the highest pressure, with a slight but definite curvature toward the pressure axis. This transformation is not only of considerable theoretical interest, but has been considered by Gutenberg (56) to be of significance in the interpretation of seismic data on the structure of the crust of the earth.

The sluggish transformation of β quartz to tridymite or cristobalite at high temperatures is of considerable interest in ceramics and thus its rate has been investigated under a variety of conditions [for example, Grimshaw *et al.* (57)]. Bridgman (58) has shown in much of his high pressure work that many substances including silicates have one or more high pressure modifications, frequently with very small volume changes. At the pressures used (up to 1,400,000 lb. per sq. in.) not only lattice transitions, but also electronic transitions may take place.

One of the most notable trends in current mineralogical systems is the increase in the determination (or calculation) and use of the thermodynamic properties of mineral compounds. This work is experimentally rather difficult because of the high temperatures and usually small heat differences involved, but solution calorimetry can frequently be used with success [Sahama & Neuvonen (59), Sahama & Torgeson (60)]. The available data are pitifully few, however, considering the complexity of most natural systems. Recent papers on measurements of thermodynamic properties include calcium and zinc silicates [King (61), Todd (62)], iron oxides [Coughlin *et al.* (63)], and geikielite, ilmenite, olivenes, and orthopyroxenes [Sahama & Torgeson (60)]. Yoder & Weir (64) have calculated the change in free energy with pressure, for the reaction $\text{NaAlSiO}_4 + \text{NaAlSi}_3\text{O}_8 = 2\text{NaAlSi}_2\text{O}_6$, from data on the density, thermal expansion, and compressibility of these compounds, in an attempt to determine the conditions under which the rather rare compound

$\text{NaAlSi}_2\text{O}_6$ (jadeite) forms in nature. Barth (65) has calculated theoretically the exsolution region in the feldspar phase diagram, and such calculations will most certainly be more frequently used in the future.

Binary Systems. Few binary mineral systems, as such, have been reported in 1951, a notable exception being the system $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 - 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ [Yoder & Keith (66)]. This system is of particular interest as an example of complete substitution of Al for Si. This might well be expected also in the system between the compounds $\text{K}_2\text{O} \cdot \text{MgO} \cdot \text{SiO}_2$ and $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$, which presumably are isostructural [Roedder (9)].

With more careful examination many compounds which were formerly considered to have integral molecular ratios are being found to have "non-stoichiometric" formulas. One of the classic examples of this behavior is the compound wüstite (FeO), which usually has compositions which must be expressed with such formulas as $\text{Fe}_{.953}\text{O}$.

Ternary Systems. A review of ternary systems up to approximately 1948 is given by Schairer (67) in a symposium on phase transformations in solids, and recent discussions of petrological application will be found in Turner & Verhoogen (68) and in Barth (69). A translation of a very useful little book by Eitel (70) summarizing phase equilibria in silicate systems is also available. Much silicate work, including high pressure, is done at the Geophysical Laboratory of the Carnegie Institution of Washington, and annual reviews of this work will be found in the Institution Yearbook [Adams (71)]. Since the publication of the 1949 supplement [McMurdie & Hall (72)] to a compilation of phase diagrams [Hall & Insley (73)], a revision of the system $\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ has been reported, revealing the ternary compound iron cordierite ($2\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) at the liquidus [Schairer & Yagi (74)]. Roedder (9) has investigated a portion of the ternary system $\text{K}_2\text{O}-\text{MgO}-\text{SiO}_2$, and has found in it four or possibly five new ternary compounds, one with the unusual composition $\text{K}_2\text{O} \cdot 5\text{MgO} \cdot 12\text{SiO}_2$, and three which appear to be isostructural with equivalent compounds in the system $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ [Schairer & Bowen (75)]. In each case it appears that substitution of one Mg^{+2} and one Si^{+4} for two Al^{+3} has taken place. Data are being obtained on the 4-component system $\text{K}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ [Schairer (76)] which should clarify the relationships between these compounds. Preliminary data would indicate the existence of solid solution between $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ (leucite) and $\text{K}_2\text{O} \cdot \text{MgO} \cdot 5\text{SiO}_2$, and between $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (kalsilitite) and $\text{K}_2\text{O} \cdot \text{MgO} \cdot 3\text{SiO}_2$. The magnesia-bearing analogues of these two minerals each appear to have several modifications which parallel those of the equivalent Al compounds [Kracek (48), Roedder (9)]. Reconnaissance work on the system $\text{K}_2\text{O}-\text{FeO}-\text{SiO}_2$ by Roedder (unpublished) indicates the existence of optically and structurally similar compounds with the formulas $\text{K}_2\text{O} \cdot \text{FeO} \cdot 3\text{SiO}_2$ and $\text{K}_2\text{O} \cdot \text{FeO} \cdot 5\text{SiO}_2$.

The ternary system $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 - 2\text{FeO} \cdot \text{SiO}_2 - \text{SiO}_2$ (leucite—fayalite—silica), a plane through the tetrahedron representing the more general quaternary system $\text{K}_2\text{O}-\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, has been studied by Roedder (77). This plane cuts through an interesting new region of low temperature

liquid silicate immiscibility in the more general system, which appears to be entirely separate from the well-known high temperature immiscibility field originating at the $\text{FeO}-\text{SiO}_2$ edge of the tetrahedron. The existence of this immiscibility is particularly significant in view of the very low slope and reverse curvature to the liquidus for fayalite in the binary system $2\text{FeO} \cdot \text{SiO}_2-\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (fayalite—albite), a join in the equivalent quaternary system with Na_2O [Bowen & Schairer (78)].

Quaternary Systems. In effect, certain portions of quaternary systems have been determined by studies of pairs or triads of compounds occurring within a more general system, for example the system luzonite—famatinitite ($\text{Cu}_3\text{AsS}_4-\text{Cu}_3\text{SbS}_4$) in the more general system $\text{Cu}-\text{As}-\text{Sb}-\text{S}$ [Gaines (79)]. In addition to the two quaternary systems mentioned in the preceding section, a part of the system $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ has been studied by Schairer & Bowen (12). A solid solution series was discovered by them between the compounds KAlSi_3O_8 and $\text{NaAlSi}_3\text{O}_8$, corresponding to the natural mineral nepheline. Since then it has become evident that the chemical composition of natural nephelines may be of considerable use in envisaging the environment from which they have crystallized [Bowen & Ellestad (80), Miyashiro (81)].

The system $\text{NaAlSi}_3\text{O}_8-\text{KAlSi}_3\text{O}_8$, a part of the anhydrous system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, has been studied by Schairer (82), and the same system, in the presence of water vapor, by Bowen & Tuttle (83). The feldspar group of minerals, consisting of these two compounds and the compound $\text{CaAl}_2\text{Si}_2\text{O}_8$, is of particular interest to mineralogists as this is by far the most abundant mineral group. Most geologists and mineralogists are interested in determining the conditions of temperature and pressure to which given rocks have been subjected in the past. The interrelationships and mutual solid solutions of these three feldspars, complicated by the existence of a number of crystalline modifications which differ only slightly from each other and which possess exceedingly sluggish transformation rates, present a problem which, by its very complexity, offers great promise in the deciphering of geological events long since discontinued.

One of the difficulties involved in the feldspar problem is the location of Al ions in the crystal lattice—whether at random, or in one of several possible ordered arrays. This location of Al ions in silicate structures has bothered x-ray crystallographers for years, as Al^{+3} usually proxies for Si^{+4} in aluminosilicates, and the two cannot be differentiated easily because of similar x-ray scattering powers. It has long been known that Ga^{+3} can replace Al^{+3} easily, presumably without significant changes in structure, and indeed there seems to be an exact parallel in structure and properties between Ga and Al compounds [Foster and Stumpf (84)]. Also it is possible to replace Si^{+4} with Ge^{+4} . These replacements of Al and Si make it possible to differentiate between Al and Si sites in the structure as a result of scattering power differences. Thus Goldsmith (85) has prepared a series of Ga and Ge feldspars in an attempt to learn more about the degree of substitutional disorder of Al and Si in the natural feldspars. Laves & Goldsmith (86) found, with the

aid of such methods, that "low" temperature anorthite (calcium feldspar), showing a superstructure which was presumably the result of ordering, by heating, could be changed continuously without a break into "high" anorthite, presumably by disordering of the Al—Si sites.

The alkali feldspars (Na and K) appear to be even more complicated. Tuttle & Bowen (87) have divided natural alkali feldspars into four series, including two forms of Na feldspar and four of K feldspar. A considerable amount of thermal, optical, crystallographic, and x-ray data have been obtained on these forms, and not all of the interrelationships are clear [see seven papers in *Journal of Geology*, Volume 58, No. 5, 1950 (82, 83, 85, 87a)], but it appears evident that ordering of Al ions is involved. Exsolution at lower temperatures of homogeneous solid solution crystals formed at higher temperatures results in numerous types of intergrowths in the natural materials [Bowen & Tuttle (83)], and may be very useful in determining the temperature at which a given rock has crystallized [Barth (65)]. At present only the high temperature forms have been synthesized in the laboratory, even in the presence of water vapor at temperatures thought to be well below the transformation temperatures. If all forms could be synthesized, the interrelationships would probably be considerably clarified.

The Na-Ca feldspars (plagioclases) are particularly common in rocks, and are characterized by certain types of crystal twinning, possibly related to the ordering process on cooling. This twinning has been under intensive study and is found to differ in various members of the series and with various types of occurrences [Gorai (88), Kaarden (89), Oftedahl (90), Turner (91)]; even now it is a useful though empirical tool for determining the conditions of origin, and is admirably suited for the petrographic method.

Quinary Systems. Only two quinary anhydrous silicate systems have been reported in the current literature: the high lime portion of the system $\text{Na}_2\text{O}—\text{CaO}—\text{Al}_2\text{O}_3—\text{Fe}_2\text{O}_3—\text{SiO}_2$ [Eubank (92)], of interest in the manufacture of Portland cement, and the feldspar join in the system $\text{Na}_2\text{O}—\text{K}_2\text{O}—\text{CaO}—\text{Al}_2\text{O}_3—\text{SiO}_2$ [Franco & Schairer (93)]. In view of the fact that most natural environments in which minerals form seldom can be considered as simple as even a five-component system, it is interesting to note the two main reasons why so little work has been done on five-component systems, and none on six-component ones. In the first place, it is difficult to determine the phase relationships in any system unless the diagrams for the limiting subsystems are available. There are five limiting quaternary subsystems to any quinary system, and as no single quaternary silicate system has ever been completely delineated, it is apparent that much ground work has to be done before most quinary systems can even be started, except for restricted ranges in composition.

Secondly, there is the severe problem of methods of representation. The phase diagram is not only a shorthand method of representing equilibrium data, but is also a powerful graphic tool for verifying equilibrium and for extrapolation or interpolation to all other compositions in the system. On a ternary TX (temperature-composition) diagram, pressure can not be repre-

sented rigorously, but only as a series of diagrams or curves, each representing isobaric conditions, as in the system $K_2O-Al_2O_3-SiO_2-H_2O$ [Tuttle (94)]. Various methods to represent the data of polycrystalline systems have been proposed [Ormont (95), Reimers (96)], but always with the aid of either simplifying assumptions or code symbols of some type. Dahl (97) has set up parametric equations for the treatment of multicomponent systems, and Mertie (98) has used "hypertetrahedra" to represent specific compositions, but while such methods are the best available, they unfortunately lack the elegant simplicity of the graphical methods so useful in unary to quaternary systems. Fortunately it is possible in many cases to alleviate the problem somewhat by limiting the four composition variables in any quinary system through the expedient of selecting three (or four) compounds containing these components. Such simplifications are exceedingly useful as long as the systems chosen remain truly ternary (or quaternary), in that any phase present can be represented in terms of the three (or four) components. Actually this is not always the case, as for example in the system $K_2O-FeO-Al_2O_3-SiO_2$, certain compositions will yield metallic iron as a phase. Crystallization paths, relative amounts of phases, etc., cannot then be obtained by the usual graphical methods, and the system becomes quinary.

The pyroxene group of minerals ($R^{++}SiO_3$) can best be represented in the quinary system $CaO-MgO-FeO-Al_2O_3-SiO_2$, in that there is a wide range of ionic substitution (solid solution) possible. Various portions of this quinary have been investigated [Hall & Insley (73)], but many of the relationships of the natural pyroxenes are unknown. Many attempts have been made to determine the nature of the system $MgSiO_3-FeSiO_3-CaSiO_3$ from careful studies of pyroxenes occurring in natural rocks, as there are systematic changes in their composition at various stages in the cooling history of a given natural melt [Muir (99)]. The system is complicated, however, by the existence of both monoclinic and orthorhombic forms, of different compositions, in many rocks.

All minerals resemble the pyroxenes above in that they are solid solutions and may take from the medium in which they crystallize various amounts of the available ions which happen to fit best their structure. The study of the crystal chemistry of minerals is a powerful tool in understanding them and is particularly useful in attempts at their synthesis for economic purposes, as with the micas. Crystal chemical studies can clarify complex phase relationships, such as the structural classification of the fluoaluminates by Pabst (100), and are needed to explain the partition of given ions between two simultaneously formed crystal structures or between a crystal structure and the medium in which it is growing. An excellent example of the trends of this partition in rocks and the conclusions that may be drawn from it will be found in Wager & Mitchell's (101) comprehensive study of the distribution of trace elements in the famous Skaergaard intrusion in East Greenland. Theoretically any such partition is temperature-dependent and may eventually be used as a "geologic thermometer" [Friedman (102)]. Such partitioning of trace elements between crystalline phases is also intimately connected

with many of the methods now existing for determining the age of rocks directly or indirectly as a result of radioactivity. (See the Annual Reports of the Committee on the Measurement of Geologic Time, National Research Council.)

SYSTEMS WITH VOLATILE COMPONENTS

Systems at Approximately Atmospheric Pressure. Volatile materials such as water may be used as components in phase equilibria studies in exactly the same manner as the "nonvolatile" oxides except that a confining pressure must be used which is equal to or greater than the vapor pressure of the system in the temperature range being investigated. Most soluble salt-water systems are determined in air at atmospheric pressure, and although the data usually do not represent true equilibrium with the air, the discrepancy is probably far less than other experimental errors.²

The application of soluble salt-water systems to mineralogy is comparatively limited. Tunell (103) has studied a portion of the $\text{CuSO}_4\text{--Fe}_2(\text{SO}_4)_3\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ system and shown its application to the leaching of copper ores, and Minguzzi (104) has applied the system $\text{CuSO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ to the problem of the concentration of copper ores in magnesian rocks. Correns (105) has examined the conditions of solution and precipitation of SiO_2 and CaCO_3 from sea water, and Rubey (106) has examined various sediment-water and water-air equilibria involved in the chemistry of sea water in an attempt to determine the geologic history of sea water. There have been many attempts to determine the environmental conditions which have yielded the complex natural saline deposits from a study of their mineral assemblages [for examples see Lang (107), Landes (108), and Armstrong *et al.* (109)]. The hardening of Portland cement involves a series of complex reactions between crystalline solids and water which have been under intensive study in recent years, as by Taylor (110).

Systems at High Pressures. One of the major advances in the field of heterogeneous equilibria as applied to mineral systems in recent years has been the rapid expansion in the use of volatile materials under pressure as components in silicate and oxide systems. These techniques have resulted in successful production of synthetic quartz crystals, much in demand for their electrical properties [Walker & Buehler (111)], and are being applied to the problem of the synthesis of many other compounds [Waesche (112)].

This advance has been essentially the result of the development of suitable apparatus and techniques, for high pressures and high temperatures, from the experimental viewpoint, are very difficult to combine. Because the rapid drop with increasing temperature in the strength of most available metals has been a severe hurdle for many years, most of the earlier work

² Most anhydrous silicate systems have low vapor pressures, even at liquidus temperatures, and hence they, too, are normally determined in air at one atmosphere, neglecting the vapor phase. As such they are usually termed "condensed systems," although this term is sometimes reserved for systems where the confining pressure is greater than the vapor pressure, thus eliminating the vapor phase completely.

has been at comparatively low temperatures and pressures. Internal heating within a bomb whose walls were kept cool made possible the combination of very high pressures (145,000 lb. per sq. in.) and high temperatures (1400°C.), as in the work of Goranson (113, 114, 115) and of Yoder (55), but involved rather extensive apparatus. Recent developments in technique, particularly that of Tuttle (94, 116) have now made it possible to subject small samples (approximately 10 mg.) simultaneously to high pressures and temperatures (e.g. 900°C. at 30,000 lb. per sq. in. for several hours) with ease and safety, using comparatively inexpensive apparatus. Use of small samples, now customary in much of the current silicate equilibrium research, might appear to be a serious handicap, but actually provides the experimenter with adequate material for phase determination by petrographic or x-ray methods and greatly simplifies many of the experimental problems. In those cases where larger samples are needed, for example where the composition of phases must be determined by chemical analysis (particularly of liquids and vapors), larger bombs must be used, usually having a modified Bridgman-type seal, and, in general, temperatures or pressures must be lower.

When temperatures or compositions are chosen which yield vapor pressures in excess of one atmosphere, not only must the equipment used be capable of withstanding the pressure, but the simplifying assumptions made for systems at atmospheric pressure cannot be used. Tunell (117) discussed the equilibria and gave a P - T - X diagram for a hypothetical binary system, showing the significance of the pressure variable. A theoretical discussion of the possible forms of such diagrams and a comprehensive review of all experiments on the synthesis and alteration of silicates by such methods up to 1937 is given by Morey & Ingerson (118). In theory both the pressure and composition of the vapor phase should be determined in all cases, but frequently in practice only its pressure is determined. This latter course is practical only in those systems where solubility in the vapor phase for the "nonvolatile" materials present is low; but even here, in order to avoid composition changes in the sample, measures should be taken to saturate the vapor phase with respect to the sample material before they come in contact, and to eliminate transfer of material by convective circulation. An ingenious technique has been developed by Bowen & Tuttle (119) for achieving these ends. In those systems where the solubility in the vapor phase is high, provision must be made for determining the composition of this vapor, as has been done by Morey (120) in the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$. Burlew has built a high pressure steam filter autoclave in which liquids may be separated from solids after equilibrating, and has determined the solubilities in portions of the system $\text{K}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ at 300°C. and 725 lb. per sq. in. [Adams (71)].

For the synthesis of compounds, not for equilibrium determinations, "hydrothermal" experiments are frequently run in which the vapor pressure of the water in the mixture upon heating is used as the internal source of pressure. This is a convenient and cheap way of obtaining high pressures, but the actual pressure developed within the bomb can only be approximated from the steam tables with a knowledge of the temperature and the "degree

of filling" of the bomb. At best this approximation is based on the frequently invalid assumption of negligible intersolubility between volatile and "non-volatile" materials, but even this approximation cannot be made in the all-too-common case in which only the total composition and the temperature are recorded with an unspecified degree of filling.

For silicate research it would be convenient in some cases to be able to add a known amount of the volatile component (e.g. H_2O) to a sample and subject the mixture to a confining pressure greater than its vapor pressure. As a consequence, no vapor phase would be present, and some of the experimental difficulties inherent in its existence would be eliminated. Furthermore, another unknown variable, the ratio of silicate to volatile in the liquid (or solid) phases, would be established by synthesis. Unfortunately this is experimentally a little troublesome, except by the sealed capsule method [Goranson (113)], and instead the volatile compound is usually pumped into the chamber surrounding the sample and the vapor or fluid phase thus maintained at constant pressure. Under this pressure an unknown, or later experimentally determined, amount of volatile material dissolves in any liquid phase present and affects the solid-liquid equilibria. Diagrams representing the lowering of the liquidus in silicate systems by water under pressure have been prepared in this way by Bowen & Tuttle (83), and as has been emphasized by them, this lowering is not due to the pressure per se, but is mainly a result of the solution of water in the liquid silicate melt, except in certain cases [Tuttle (94)]. This solubility of volatile material in the melt obviously is dependent on pressure, temperature, and composition.

Research on another important unknown, the solubility of "non-volatile" materials in the vapor phase, has resulted in data of extreme importance to the geologist and mineralogist, particularly through the work of Morey (120). He has shown that "nonvolatile" materials such as silica can "dissolve" in the vapor phase to a remarkable degree, at geologically moderate temperatures and pressures. For example, Morey & Hesselgesser (121) were able to obtain homogeneous gases at 30,000 lb. per sq. in. with densities near 1.4, having over 24 per cent Na_2O and 8 per cent SiO_2 at temperatures in the range 400–500°C. and other experiments indicate that in certain cases over 50 per cent by weight of such solid materials may exist in solution in the vapor at temperatures from 375° to 500°C. and pressures up to 16,500 lb. per sq. in. [Morey (120)]. It is thus evident that the pressure-temperature-volume relations recently determined for pure water at pressures up to approximately 36,000 lb. per sq. in. and temperatures up to 1000°C. [Kennedy (122)] must be considerably modified by dissolved materials in the system $Na_2O-SiO_2-H_2O$.

This solubility for a given material in the vapor phase is, however, exceedingly dependent upon the composition of the system. In contrast with the above data, Morey & Hesselgesser (121) found the solubility of pure SiO_2 in pure water vapor, using a dynamic method and special care to insure saturation, to be only 0.26 gm. SiO_2 in 100 gm. H_2O at 500°C. and 15,000 lb. per sq. in. water pressure (density 0.54). In addition to the variation in

solubility in the gas phase with composition, the solubility is also pressure-dependent. Kennedy (123) found that the solubility of SiO_2 in water vapor at constant temperature was almost a direct function of the density of the vapor phase, and hence of the pressure. The critical temperature of water, in the system $\text{K}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ [Morey & Fenner (124)], was found to be without influence on the series of isothermal polybaric saturation curves from 200° to 600°C .

Most environments in which minerals have formed from natural silicate melts (magmas) involve comparatively high pressures and at least small amounts of volatile compounds such as CO_2 and particularly H_2O in solution in the melt. The effects of such materials on the equilibrium diagrams, although frequently large in proportion to the quantity present, are not so large and unpredictable as is sometimes thought. For example, Bowen & Tuttle (83) found that the presence of 7.5 per cent H_2O (at 14,200 lb. per sq. in.) in an intermediate composition in the system $\text{KAlSi}_3\text{O}_8-\text{NaAlSi}_3\text{O}_8$ (the alkali feldspars) resulted in a lowering of the liquidus and solidus by 220°C . As more or less a parallel to this case, in anhydrous systems, Roedder (9) found that the presence of 11.5 per cent K_2O in certain compositions in the system $\text{MgO}-\text{SiO}_2$ resulted in a lowering of the liquidus 378°C . below the lowest temperature on the liquidus in the pure $\text{MgO}-\text{SiO}_2$ system, and similarly in the diagram for the system $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ [Schairer & Bowen (75)] the addition of K_2O , in the amount of 9.5 per cent of the mixture, to certain compositions in the system $\text{Al}_2\text{O}_3-\text{SiO}_2$ can result in a lowering of the liquidus by almost 700°C . Thus water (and other volatile materials) as far as its effect on equilibrium is concerned, may be considered to be merely another component that happens to require pressure to keep it in the melt.

In distinction to its effects on equilibria, the effect of water or other volatiles on those physical properties of silicate materials involving rate processes, such as viscosity, nucleation, crystallization, and even melting, is far in excess of that which might be expected in view of their concentration. Thus in the system $\text{KAlSi}_3\text{O}_8-\text{NaAlSi}_3\text{O}_8$, Schairer (82) obtained only partial crystallization of anhydrous liquids (glasses) of these compositions in several years, at optimum conditions for crystallization. Bowen & Tuttle (83), using the identical samples, were able to obtain complete crystallization in hours under 4250 lb. per sq. in. water pressure. The melts under these conditions probably contained considerably less than 7 per cent H_2O , on the basis of the determinations made at higher pressures. Actually the quantity of volatile materials in the melt needed to effect large changes in rate processes such as nucleation and growth of crystals may be exceedingly low under some conditions. Thus Roedder (9) found that the presence of an unknown quantity, considerably less than 0.5 per cent, of a mixture of volatile materials was effective in causing crystal nucleation and considerable crystal growth, in hours, in compositions that stubbornly refused to initiate crystallization, even when "seeded" with the correct crystalline phases, in months under optimum conditions without such volatile materials [see also Greig

& Barth (125)]. The explanation for such tremendous rate effects probably lies in the reduction of the number of Si—O—Si bridges in the polymerized silicate liquid structure as a consequence of the lower charge on the (OH) ion [Buerger (126)].

In addition to the above-mentioned systems including water, three ternary systems have been reported recently: MgO—SiO₂—H₂O [Bowen & Tuttle (119)], Al₂O₃—SiO₂—H₂O [Roy & Osborn (127)], and MgO—Al₂O₃—H₂O [Roy & Osborn (128)]. Data on such systems are usually presented in the form of PT curves for each reaction of crystalline phases and vapor representing univariant equilibria, and as an isobaric series of sets of composition triangles, each set representing phase relationships for the whole system in a given temperature range. Friedman (129) has reported finding several new compounds with very unusual compositions (molecular ratios of Na₂O:Al₂O₃:SiO₂:H₂O being 13:9:22:12 and 28:19:42:24, respectively) in the system Na₂O—Al₂O₃—SiO₂—H₂O.

Yoder (130) has explored phase equilibria in a portion of the system MgO—Al₂O₃—SiO₂—H₂O at temperatures from 450° to 900°C. and at water vapor pressures up to 30,000 lb. per sq. in. This study is of considerable significance to the geology of the metamorphic rocks. Metamorphic rocks (those which have been recrystallized or changed from their original mineralogical composition while deep in the earth) usually consist of several crystalline phases which have in the past, in most cases, been in equilibrium with each other at elevated temperatures, under high confining pressures (overlying rock load) and with an unknown but significant amount of water present. With a given chemical composition rock, this assemblage will vary with the magnitude of the temperature and the pressure to which it has been subjected (i.e., the "metamorphic grade"). As such, the mineral assemblages or "facies" may be used to determine, within limits, the conditions of temperature and pressure under which the rocks were formed, and as a consequence, may help in the understanding of large scale structural features in some areas [for example see Kennedy (131)]. The method has serious limitations, however, resulting from such factors as the wide variation in composition of the natural "systems," high shearing stresses, availability of water [Yoder (130)], later changes upon lowering of temperatures or pressures ("retrograde metamorphism"), etc. A considerable literature exists on attempts to evaluate these factors. Certain rock types, for example the siliceous limestones and dolomites [Tilley (132)], are particularly useful in that there are many possible phases, yet the components are few. Even here, however, the application is limited by the magnitude of the loss of carbon dioxide [Danielsson (133)], and in cases where materials are added to such rocks during metamorphism, as for example boron and fluorine [Tilley (134)], an entirely new suite of minerals containing these elements may develop.

Bowen & Tuttle (135) have investigated the subsystem NaAlSi₃O₈—KAlSi₃O₈—SiO₂—H₂O in the more general quinary system Na₂O—K₂O—Al₂O₃—SiO₂—H₂O at water pressures up to approximately 43,000 lb. per sq. in. and temperatures up to 1000°C. The results of this work are of vast

significance to geologists in that many common rock types (e.g. granite, syenite, etc.) can be considered to fall in this system, except for minor amounts of other components, and hence the laboratory work can be applied almost directly toward explaining conditions of formation of the natural phase assemblages.

CERAMIC SYSTEMS

The engineering specifications of new materials desired for the development of heat engines, electronics, nucleonics, etc., have imposed a new and vital interest in ceramic products. In the development of these the study of phases and phase transitions is of paramount importance.

The value of using reactions in the solid state in phase equilibrium research as a reconnaissance into the character of ceramic systems, and the nature of the useful information such an approach can yield, is reviewed by Foster (136). It is contended that the often repeated statement that solid state reactions seldom go to thermodynamic equilibrium is false, and that many workers give undue importance to the primary phase fields in ternary systems and give insufficient attention to the compatibility triangles (composition triangles). Foster also discusses the influence of melting intervals on firing ranges, the nature of crystallization paths, and the importance of distinguishing between the types of invariant points.

The phases of the boride systems of cerium, titanium, zirconium, columbium, tantalum, molybdenum, and uranium were studied by Brewer *et al.* (137). Tungsten and molybdenum each form three solid phases with boron, four of which have appreciable solid-solution ranges; tantalum and columbium each form five solid phases with boron, several of which have significant solid-solution ranges; zirconium, titanium, and thorium each form one solid phase with boron; and cerium and uranium each form two. A number of these phases have been reported heretofore, but since the work on these systems is far from complete and these substances have refractory possibilities, this contribution is timely.

An interesting study by Bauer & Gordon (138) on the flame-fusion synthesis of certain silicates has demonstrated the production of such incongruent melting phases as mullite, clinoenstatite, and lithium disilicate. If these results are confirmed they should furnish data for interesting crystallization rate studies. Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is an important phase in the fired aluminum silicate ceramics, hence its stability is of prime importance in these products. Gad & Barrett (163) have studied the effect of the alkalis and alkaline earths on the destruction of this phase.

In the system $\text{ZrO}_2\text{—TiO}_2\text{—SiO}_2$, studied by Sowman & Andrews (139), the binary system $\text{ZrO}_2\text{—TiO}_2$ showed no compounds. Solid solutions of up to 21 per cent ZrO_2 in TiO_2 and 37 per cent TiO_2 in ZrO_2 , and a eutectic at 1600°C. were found. The ternary system has no compounds but has a eutectic located at 1500°C. with 2-ZrO_2 , 10-TiO_2 , and 88-SiO_2 . A small furnace which permitted x-ray diffraction studies to be made up to 1750°C. was designed for this study.

Several polymorphic forms of magnesium metasilicate, the crystalline ingredient in the steatite ceramics so extensively used as insulators in high frequency electrical equipment, are known to exist. Foster (51) has made a new study of this material and proposes that protoenstatite (mesoenstatite) is the high-temperature form and that this can reversibly transform to clinoenstatite in a manner similar to the α - β transformation of cristobalite. Clinoenstatite under the influence of catalysts and at low temperatures probably reverts very slowly to enstatite, which on heating will transform to protoenstatite at 1260°C. It is not certain that the nature of the magnesium metasilicate phases has been finally elucidated by this study.

The phase diagram of the TiO_2 - SiO_2 system has been further studied by Ricker & Hummel (140) with the result that extensive changes from the presently accepted diagram are proposed. The composition of the eutectic is shown to exist at 21 per cent titania rather than 10 per cent as heretofore supposed. Considerable solid solution is found to exist at both ends of the system, and the α - β inversion temperature of cristobalite with 10 per cent titania in solid solution was found to be altered from 275°C. to 130°C.

Celsian ($\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) has been synthesized by Yoshiki & Matsumoto (141). A hexagonal modification exists at high temperatures which reverts to the normal monoclinic celsian at low temperatures, and an α - β transformation at about 300°C. was also shown.

The solid-state reactions in the system MgO - ZrO_2 - SiO_2 , studied by Foster (142), indicated that at least four invariant points exist. The earlier results of other workers are thrown into doubt because the presence of a proposed ternary compound could not be confirmed and a solid-state reaction reported not to exist below 1540°C. was shown to take place at temperatures as low as 1240°C.

Although the quaternary system MgO - CaO - Al_2O_3 - SiO_2 is very important in the refractory industry, the complexity of a four-component system is such that the technical needs are considerably in advance of the phase information. Prince (143), in a detailed study of the ternary join MgO - Al_2O_3 - Ca_2SiO_4 in this system, found four binary and two ternary eutectic systems.

Dudavskii & Ioselzon (144) in a theoretical study of the possibility of a solid solution replacement of 2 Si^{4+} by 2 $\text{Al}^{3+} + \text{Fe}^{2+}$ have deduced that if such a solid solution will form, then the rapidity of the reaction cristobalite \rightarrow tridymite should be substantially increased. If the substitution of 2 $\text{Fe}^{3+} + \text{Fe}^{2+}$ for 2 Si^{4+} is possible, then the rate of transformation should be still further increased. Since the use of silica as a refractory is largely based on the favorable properties of the tridymite phase, an experimental investigation of this suggestion in extended form might have interesting and important technical results. Using the effusion method, Schäfer & Hörnle (145) have found the vapor pressure of silicon monoxide over mixtures of silicon and silicon dioxide to be 23.8×10^{-3} to 263.2×10^{-3} mm. Hg from 1336° to 1460°K., and the vapor pressure of germanium monoxide in the system Ge - GeO - GeO_2 has been determined by Bues & Wartenberg (146) between 900° and 1000°K.

Interesting polymorphic modifications of silicon carbide are still being found. Taylor & Laidler (147) have determined the conditions under which the β cubic, face-centered cubic, and hexagonal II forms are produced, and have shown that the face-centered cubic modification transforms to graphite and the hexagonal II modification at approximately 2000°C. Greenhouse *et al.* (148) have found TiC to react with B₄C at high temperatures to form TiB₂ and carbon. Another titanium boride is presumed to form in small amounts, but was not identified. Dawihl & Schräter (149) have studied the WC—Co system and have shown that at 1300° C. the solid solution of Co in WC is less than 1 per cent and the solid solution of WC in Co is approximately 7 per cent.

The solid solutions of γ -Fe₂O₃ with γ -Al₂O₃ have been studied by Cirilli (150) and of β -Fe₂O₃ with β -Al₂O₃ by Cirilli & Brisi (151), demonstrating complete solid solubility of Al₂O₃ and Fe₂O₃ down to room temperature. The Al₂O₃ in a solid solution Al₂O₃—Fe₂O₃ (50:50) can be dissolved in strong sodium hydroxide with the magnetic susceptibility of the residue increasing up to an Fe₂O₃ content of 90.4 per cent, then decreasing abruptly. X-ray analysis showed this Fe₂O₃ to be γ phase up to the break, above which the presence of a rhombohedral form was found. The γ form of Fe₂O₃ is stabilized by a small quantity of Al₂O₃, the β form of these materials being stabilized by crystallizing with a small quantity of K₂O forming K₂O·11Fe₂O₃ and K₂O·11Al₂O₃. From magnetic susceptibility measurements it is inferred that two solid solution series are formed and that solid immiscibility exists between β -Al₂O₃ and β -Fe₂O₃ when the latter is in excess of 55 per cent.

In their investigation of the analogies between gallia and alumina, Foster & Stumpf (84) observed the only hydrate of gallia to be isomorphous with diaspore (Al₂O₃·H₂O). The form of gallia isomorphous with α alumina, (corundum) is produced only by dehydrating the "fully developed" gallia hydrate. The compound Na₂O·11Ga₂O₃ was found to be analogous to so-called β alumina (Na₂O·11Al₂O₃), and all the observed crystal phases of gallia have a counterpart in alumina except for the temperature reversal of the theta and alpha forms. As might be expected, extensive solid solution is shown to exist between all comparable gallia and alumina phases.

Zirconium oxide has potential refractory uses if and when it is stabilized against transformation. Duwez *et al.* (152), in studying the stabilizing influence of Y₂O₃, found its addition to ZrO₂ in solid solution lowers the tetragonal→monoclinic transformation in relationship to the amount of Y₂O₃ added up to 6 mole per cent, above which value the ZrO₂ is stabilized against transformation. Two solid solutions are formed at 2000°, one with from 7 to 55 mole per cent Y₂O₃, the other with from 76 to 100 mole per cent. The ZrO₂ lattice is stable with a defect in the oxygen sites, and the Y₂O₃ lattice can accommodate excess oxygen. Experiments with scandia, samaria, and gadolinia show that these earths have similar effects upon zirconia.

The Zr—ZrO₂ system has been investigated by Cubicciotti (153). The temperatures were computed from optical pyrometer readings, using emissivities which are not too well known. The solidus curve derived from the data is such that one would like to see the liquidus curve also for a full

understanding of the system. No evidence was found for the existence of ZrO , although this compound has heretofore been postulated to exist. It was found that ZrO_2 may take up to 15 mole per cent of Zr metal into solid solution, seeming to confirm the observations of Duwez *et al.* (152). Solid solutions of thoria and lanthana also have been shown by Hund & Durwachter (154) to have a defect in the oxygen lattice similar to that of ZrO_2 .

Strauss *et al.* (155) have investigated the Ba—Co—O system. Three heretofore unreported phases were found, the formulas for which are $\text{BaCoO}_{2.72}$, $\text{BaCoO}_{2.31}$, $\text{BaCoO}_{2.23}$. These phases were free of contaminating phases only when the atomic ratio of barium to cobalt is one. An attempt is made to explain the cause of the oxygen deficiency from the expected stoichiometric compositions. It is quite evident that more information on this system is needed before a full elucidation is possible. In the system BaO—NiO [Lander (156)], two solid phases $\text{NiO} \cdot \text{BaO}$ and $\text{NiO} \cdot 3\text{BaO}$ were observed. Lander & Wooten (157) extended this study by adding oxygen, and observed that the phase BaNiO_3 when heated from 730° to 1200° gave off oxygen, resulting in a solid with a range of composition from $\text{Ba}_3\text{Ni}_3\text{O}_8$ to $\text{Ba}_2\text{Ni}_2\text{O}_5$.

The binary system UO_2 —CaO [Alberman *et al.* (158)] shows a eutectic at $2080^\circ \pm 20^\circ$ at 45 mole per cent of UO_2 , and the compounds Ca_2UO_4 and CaUO_3 . CaO does not take UO_2 into solid solution, but the UO_2 will take in CaO, yielding a defective fluorite structure containing 47 mole per cent CaO at the eutectic temperature.

The system FeS—FeO— SiO_2 has been investigated by Ol'Shanskii (159). FeS has little solid solubility in SiO_2 , even at temperatures near the melting point. No SiO_2 was found in the FeS phase, but a eutectic exists at 920°C . with the approximate composition 65-FeS, 35-FeO, and $<1\text{-SiO}_2$, a diagram of the liquidus surface being given which is based on the results of a study of 15 compositions. The binary FeS—FeO was treated as the Fe—FeS—FeO ternary system, a ternary eutectic being found at 920° with a composition 65-FeS, 30-FeO and 5-Fe. With excess oxygen and sulfur the eutectic temperature rises to 1000° .

Zoja (160) in a study of the ternary system Cr_2O_3 —FeO— SiO_2 has confirmed the complete immiscibility of SiO_2 and Cr_2O_3 . Four binary eutectics (minima) between Cr_2O_3 and FeO were observed, suggestive of the possibility of three compounds between these two constituents. Chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) is known, but further information on the other two would be interesting.

The quaternary system MgO—CaO— TiO_2 — SiO_2 was investigated by Berezhnoi (161). In the CaO—MgO— TiO_2 ternary both CaTiO_3 and MgTiO_3 are formed simultaneously in a solid state reaction. An excess of CaO results in the initially formed CaTiO_3 (perovskite) reacting with CaO above 1400° to form a more basic titanate. Mg_2TiO_4 is formed only at temperatures in excess of 1500°C ., and is a highly refractory material whose softening point is very sensitive to small quantities of silicate. The lowest melting ternary eutectic in this system is at 1400°C . and has an approximate composition of 15-CaO, 12-MgO, 73- TiO_2 . The perovskite is reported to be capable of

coexisting with CaTiSiO_6 , CaSiO_3 , $\text{Ca}_3\text{Si}_2\text{O}_7$, and CaSiO_4 . The eutectic temperature of $\text{CaTiO}_3\text{--Ca}_2\text{SiO}_4$ is 1660°C . and contains about 33 per cent of the latter compound. In the system $\text{MgO--TiO}_2\text{--SiO}_2$ the formation of a ternary compound was not observed. The ternary CaO--MgO--SiO_2 was studied again.

Statton (162) has investigated the entire BaO--TiO_2 system and has shown the existence of four primary solid phases represented by the compounds BaTi_4O_9 , BaTi_2O_6 , BaTiO_3 , and Ba_2TiO_4 . While this contribution is a significant advance in the information regarding this system, it appears there is much work yet to be done. An interesting feature of this work is the development of a micro melting furnace to investigate high melting ceramic mixtures in quantities less than 1 mg.

PHASE TRANSITIONS IN SOLIDS

Intensive investigations of the phase transitions in solids are now taking place in many academic and industrial laboratories. The technological importance of such transitions in determining the properties of alloys, ferro-magnetic materials, solid dielectrics, piezoelectric materials, semi-conductors, specialized ceramics, optical components, etc., will assure that this type of research is increased. This development is emphasized in this review because in the past this field of heterogeneous equilibria, except perhaps in the case of metal alloys, has not been extensively studied.

Several systems of nomenclature have been developed by independent workers in a variety of specialized fields interested in solid-state transformations. The physical chemists [Mayer (164)] have adopted a nomenclature consistent with the mathematical formulation of the thermodynamic properties; abrupt transformations in the extensive properties of the solid (energy, volume, entropy, etc.) are called "first order," those in the first derivatives of the extensive properties are called "second order," etc. The physicist has been especially interested in electrical conductivity, magnetic susceptibility, and dielectric behavior, and has called transitions affecting these "Curie points" or "Curie temperatures." The heat capacity versus temperature curves of many substances have characteristic breaks reminiscent of the Greek letter lambda; hence these are spoken of as "lambda transitions" [Kracek (48)].

Following the work of Bragg & Williams (165) many transitions in solids are referred to as "order-disorder transformations." In order to focus attention on the mechanistic and structural nature of transitions Buerger (49) has proposed the following classification scheme:

- I. Transformations of Secondary Co-ordination (Network transformations)
 - Displacive (high-low, rapid)
 - Reconstructive (sluggish)
- II. Transformations of Disorder
 - Rotational (rapid)
 - Substitutional (sluggish)

III. Transformations of First Co-ordination

Dilatational (rapid)

Reconstructive (sluggish)

IV. Transformations of Bond Type

(usually sluggish)

To emphasize experimental observations Kracek (48) has proposed the descriptive term "gradual transitions" for transitions of the α - β type such as are characteristic of silica. A term "transition of the second kind" (distinguished from transitions of the second order) is introduced by Tisza (166) to be used for certain critical points. Thomas & Stavely (167) classify phase transitions into three types depending upon whether the temperature characteristic of the change is continuous over a wide range of temperature, or isothermal, or is a mixture of these two.

Ferroelectric substances (also called Rochelle-electrics or Siegnette-electrics) are characterized by abnormally high dielectric constants. They display co-operative effects and hysteresis in dielectric properties which are analogous to those of ferromagnetic materials. The first substance observed to possess the ferroelectric property was Rochelle salt ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), which has two transitions confining the ferroelectric phase between the temperatures of -18°C . and $+24^\circ\text{C}$. Ferroelectric substances have always been observed to possess piezoelectric properties of interesting magnitude.

In a review of recently observed phase transitions in ferroelectric substances Matthias (168) pointed out that Rochelle salt was unique in that it was the only ferroelectric substance then known which shows phase transitions on both ends of a temperature range wherein the ferroelectric phase exists. Since this publication, it has been found by Shirane *et al.* (169) that solid solutions of up to 15 mole per cent PbTiO_3 in PbZrO_3 also show two phase transitions which limit the ferroelectric phase between temperature boundaries. Still more recently Shirane (170) has found that solid solutions of either BaZrO_3 or SrZrO_3 in PbZrO_3 show the same phenomena. An interesting feature of these systems is that below the lower transition temperature they become antiferroelectric. The specific heat of lead titanate near the upper temperature boundary of the ferroelectric phase was shown by Shirane & Sawaguchi (171) to have a broad anomaly from 350°C . to 525°C . with a sharp peak at 490°C . The existence of a latent heat at the transition point (490°C .) has not been determined.

Further detailed study of the ferroelectric properties and phase transitions in barium titanate (BaTiO_3) have been made. Merz (172) has shown that the ferroelectric phase of this material persists down to liquid helium temperatures. It has been determined by Statton (162) and confirmed by Wood (174) that a high-temperature, noncubic phase exists above about 1460°C . Edwards *et al.* (175) have demonstrated that the cubic perovskite structure is retained up to 1372°C .

The transitions which bound the stable ferroelectric phase regions have been compared by Tisza (166) for the substances Rochelle salt, potassium dihydrogen phosphate, and barium titanate. He points out that the nature

of these transitions is such that each must be considered as distinctively different from the others.

Several new ferroelectric materials were reported and their phase transitions observed. A ferroelectric phase in lithium ammonium tartrate monohydrate was independently discovered by Matthias & Hulm (176) and by Merz (177). The first investigators found an upper transition temperature at 98.5°K; the latter investigator at 106°K. No lower transition temperature was found by either. Matthias & Hulm (176) also found lithium thallium tartrate monohydrate to be ferroelectric with an upper transition temperature at 10°K. and no observed lower transition down to 1.3°K. Further information on the recently discovered ferroelectric sodium and potassium columbates was obtained by Matthias & Remeika (178). The potassium columbate has a transition temperature at 434°C. and another at 220°C. Three phase changes were noted in sodium columbate at 480°C., 370°C., and -80°C., respectively.

The phase transitions in ferroelectric WO_3 were further elucidated by Ueda & Ichinokawa (179). The transformation is not sharp but takes place in a temperature range from 700° to 750°C. The lattice constants have a discontinuity near 700°C. and a volume and significant energy change at about 720°C. Sawada *et al.* (180) found the transition temperature to be 710°C. on heating and 685°C. on cooling, with a lambda-type volume transition.

Smart & Greenwald (181) have shown that manganous oxide, ferrous oxide, calcium oxide, and nickelous oxide are substances which have antiferromagnetic phases. Above their Curie points each possesses the NaCl structure and is paramagnetic; below, each becomes antiferromagnetic with calcium oxide assuming a tetragonal symmetry, and the other oxides a rhombohedral symmetry. Greenwald (182) has shown that chromic oxide is antiferromagnetic with a Curie temperature at 314°K. and with the magnetic dipole directions the same in each 111 plane and alternate in successive planes. A similar transition in magnetite at 95°K. has been shown to exist by Tombs & Rooksby (183). The phenomenon of antiferromagnetism has been discussed theoretically by Slater (184), who also has an interesting explanation of the increase in resistivity at very low temperatures for some metals [Slater (185)] in terms of a phase change of the above type. Nickel ferrite exhibits increased electrical resistivity and an anomaly in magnetic susceptibility in a phase region bounded by -120°C. and -195°C. [Okamura (186)].

A phase transition leading to rotation of certain groups in barium dicalcium propionate has been studied by Seki *et al.* (187). The specific heat curve, however, shows two maxima with hysteresis, suggesting a phase transition in two discrete steps. As lead is added as a partial replacement for barium, the small peak becomes sharper, shifts towards the large peak, and finally merges with it.

Thomas (188), in studying the λ point of ammonium chloride, has found that the hysteresis loop for the transition decreases as the particle size decreases, and that the temperature of the λ point is increased slightly more than 2° for each substitution of a deuterium for a hydrogen.

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PHOTOCHEMISTRY¹

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The physical chemist is interested in the use of light to cause chemical reactions to occur because in this way he is able to study the properties of various reactive substances which are of importance in the detailed mechanisms of many reactions. Light is also of use in the preparation of certain specific compounds or as an easy means of increasing the rates of certain reactions which lead to the production of desired substances. In this review there has been no attempt to cover this preparative aspect of photochemistry although it is realized that such information may be of great importance to many chemists. The material presented here is limited to that which is concerned with the determination of the nature of the reactive intermediates formed by the action of light and a study of the secondary reactions between these intermediates or of these intermediates with other substances.

REACTIONS OF RADICALS

Several papers have appeared in which the principal interest has been in the reactions of photochemically produced radicals. Trotman-Dickenson & Steacie (1), in a paper with 39 references, review work on the relative efficiencies of the two reactions



Their general conclusion is that, except when RH is acetaldehyde, the reaction of type 1 has a steric factor about 10^{-3} or 10^{-4} of that for reaction 2. The same conclusion has been reached by Dorfman & Gomer (2) in an earlier review but Evans & Szwarc (3) claimed that the steric factors in reactions of this type are essentially "normal," that is, not greatly different from unity. Gomer & Dorfman (4) in challenging this statement and the work of Szwarc & Roberts (5) have pointed out that the data used by the latter authors can be treated so as to lead to the conclusion that the steric factors are about 10^{-3} or 10^{-4} . Szwarc (6) believes that the differences are merely a matter of what assumptions are used and stresses that in the previous papers the only claim which has been made is that the collision frequencies times the probability of reaction (PZ) for these reactions are of the order of 10^{11} to 10^{12} and that this value is of the same order as is observed for bimolecular reactions of ordinary molecules. Although there are some uncertainties in the interpretations of the experimental data if one accepts the idea that the relative

¹ The survey of the literature pertaining to this review was concluded in January 1, 1952.

amounts of methane and ethane formed represent the relative amounts of the reactions 1 and 2, it is hard to avoid the conclusion that in terms of the collision theory approach the ratio of the steric factors is of the order of 10^{-3} or 10^{-4} .

The absolute value of the steric factors for reactions of the type 1 is still open to question because of the great disagreement concerning the magnitude of the rate constant for reaction 2. It seems that it is generally conceded that the activation energy for 2 is zero within the limits of the observations which have been made but there the agreement ends. Miller & Steacie (7) compared the rate of 2 with that of the reaction of methyl with nitric oxide. On the basis of their results and Forsyth's (8) value for the rate constant of the reaction of methyl with nitric oxide, they conclude that the collision yield for the reaction of methyl with methyl is 4.4×10^{-5} .

In contrast to the work just cited we find that the results obtained by Dodd (9) with acetaldehyde lead to the conclusion that methyl radicals combine with each other at every collision. The same conclusion was reached by Gomer & Kistiakowsky (10) from the studies of the photolysis of mercury dimethyl and acetone by intermittent light. They used sufficiently high light intensities so that the ratio of the amount of ethane formed to the amount of methane formed was always at least 10. Under these conditions the amount of methane formed served as a measure of the concentration of methyl radicals so that the rates of formation of methane in steady illumination and with intermittent light gives the ratio of the methyl radical concentrations under the two sets of conditions. The final result obtained in this way is that the rate of combination of methyl radicals to form ethane is 4.5×10^{13} (moles/cc.) $^{-1}$ sec. $^{-1}$ with an activation energy of 0 ± 700 regardless of the radical source. This value actually corresponds to an effective collision diameter of less than one Angstrom which suggests that some collisions do not result in reaction. However, Dodd's value is larger and corresponds more nearly to reaction at every collision from the classical point of view. Both values are close enough to the collision frequency to justify the statement that reaction occurs at essentially every collision. Gomer & Kistiakowsky point out that in their experiment it seems quite improbable that the rate constant would be the same for the two reacting systems if the ethane were actually being formed by some other reaction than the assumed combination of methyl radicals. They discuss some other mechanisms and point out the difficulty of reconciling them with the experimental facts.

Marcus & Rice (11) have discussed the combination of methyl radicals and iodine atoms from a theoretical point of view and tentatively infer that the collision efficiency for the formation of methyl iodide varies from 0.001 to 0.01 as the total pressure is increased from 20 mm. to infinity. Their discussion is based on various assumptions as to the nature of the activated complex. Such a calculation may be sound in principle but is faced with tremendous difficulty in defining the activated complex. For reactions which have an activation energy the activated complex is the system at the crest of the potential barrier which must be surmounted for the reaction to pro-

ceed. However, the reaction between a methyl radical and iodine atom to form methyl iodide is supposed to proceed without any activation energy; hence, the interaction between the two radicals begins at relatively large distances and increases up to the condition corresponding to formation of the addition product. Marcus & Rice assume various degrees of coupling in their discussion of what constitutes the activated complex. The problem is entirely analogous to the reaction of two methyl radicals except that one of the reacting groups is a single atom. This difference may be enough to reduce the probability of combination to the fraction cited by them. If so, experiments on methyl iodide with very high light intensities, such as are provided by the flashes described by Porter & Norrish (12), should yield a relatively high amount of decomposition at low pressure since a large amount of the iodide will be split into methyl radicals and iodine atoms and the former will combine to form ethane rather than recombine with the iodine atoms.

Osugi (13, 14) has attempted to study the rate of combination of methyl radicals and also of a methyl radical and iodine atom by following the small change in pressure which occurs after a brief period of illumination of methyl iodide. He concludes that both reactions are bimolecular and occur at essentially every collision. Actually about the only conclusion which his results seem to justify is that the intermediates disappear by a bimolecular reaction which occurs at essentially every collision, but he does not seem to have data sufficient to differentiate between the two possible reactions.

It is essentially impossible to make a decision concerning the magnitude of the "steric" factor for these reactions on the basis of the simple collision theory since there is no way to calculate how precisely two molecules have to be oriented to react or what is the probability that a reaction will occur if the right orientation exists. The approach of the "absolute rate" theory offers a mechanism for such a calculation through the estimation of entropies of activation. These entropies can be thought of in terms of the restrictions or changes in restrictions which occur in the formation of the activated complex. This is the type of calculation made by Marcus & Rice, but it is not necessary to make the specific assumptions they have made. The minimum condition which we can impose is that two molecules in order to react must be within the same reasonably small element of volume or in other words must be within some more or less fixed distance of each other. This statement is equivalent to eliminating one degree of freedom with respect to translation. Since the translational entropy of a molecule is usually about 30, the elimination of one degree of freedom can be expected to result in a decrease in entropy of about 10. With such an entropy of activation the absolute rate theory yields the same value for the frequency factor of a bimolecular reaction as is calculated from collision theory assuming reaction at every collision. The maximum restriction associated with the formation of the activated complex, other than quantum effects which affect the transmission coefficient, would be that which could be referred to as the two reactants forming a firmly bonded molecule. In this case the major, if not only, entropy change is the loss of the translational entropy of one molecule, that is, a

decrease of about 30. Such a decrease corresponds to steric factor of about 10^{-4} on the collision theory basis. Now there seems to be general agreement that the hydrogen abstraction reactions of type mentioned have steric factors 10^{-3} to 10^{-4} that for the combination of two methyl radicals. The combination of these two statements leads to the conclusion that two methyl radicals must combine with each other at essentially every collision. The only way smaller steric factors could occur would be for some quantum restriction to reduce the transmission coefficient below unity. Although such a condition could exist, it seems highly improbable that so many reactions would have small but practically identical transmission coefficients (15, 16, 17).

Nicholson (18) has used the photolysis of acetone to study the effects introduced by the diffusion of methyl radicals out of the light beam in experiments in which the beam did not cover the entire cell. In a cell of 1.8 cm. diameter it was found that diffusion effects may be neglected provided that the temperature is above 100°C . and the acetone pressure above 100 mm. The small effect present under these conditions becomes more marked as the size of the light beam is reduced. At lower temperatures the radicals diffuse out of the beam to such an extent that at 26°C . it is necessary to use the cell volume instead of the light volume in calculations. The agreement between theory and experiment is qualitative or at best semiquantitative. For accurate calculations it is necessary to know the rate constants for the various steps in the mechanism even better than they are known for acetone; hence in most systems it will be necessary to make experimental tests to determine whether or not diffusion is important.

Linnell & Noyes (19) have studied the behavior of pyridine and mixtures of pyridine and acetone when illuminated with various ultraviolet wave lengths. They found that the methyl radicals produced from the acetone did not extract hydrogen from pyridine to form methane even at temperatures up to 210°C . The pyridine itself was not decomposed appreciably by light absorbed in the first banded region in the ultraviolet but did undergo some decomposition when illuminated with wave lengths shorter than 2537 \AA . This decomposition was not investigated in detail.

Noyes (20) has discussed the behavior of radicals and activated molecules in photochemical systems with particular reference to those in which acetone or benzene is the absorbing substance. Much of the paper is a review of previous work, but some new work, especially with benzene, is reported. It was found that no reaction occurred between photoactivated benzene and hydrogen, oxygen, hydrogen chloride, and nitrous oxide. Negative results of this type are of value in that they serve to impose limitations on the kinds of elementary processes which can be assumed in cases where there is a reaction.

Brinton & Volman (21) have postulated the existence of the ethylidene radical in the photolysis of diazoethane. They cite in support of this assumption the formation of a small amount of butene. The relatively large amount of ethylene found could be formed by the rearrangement of the ethylidene radical or it might result from the direct formation of ethylene and nitrogen by a different primary decomposition. The work was not complete enough

to distinguish between the two possibilities, but it might be pointed out that if the ethylene is formed by the latter method the relative amount of butene-2 and ethylene should be independent of the light intensity but if the other mechanism holds the amount of butene-2 formed should increase relative to the ethylene as the light intensity is increased.

W. H. Urry & Eiszner (22) reported that on illumination of mixtures of diazomethane and carbon tetrachloride 1,3 dichloro-2,2 *bis* (chloromethyl) propane was formed. If bromotrichloromethane were substituted for the carbon tetrachloride one chloromethyl was changed to a bromo-methyl group. The most reasonable means to account for this observation is to assume that methylene radicals are formed from the diazomethane and these react with the tetrahalide. If this is really the mechanism, it is surprising that none of the possible intermediate products were reported.

Hamill & Schuler (23) have discussed the photolysis of liquid methyl and ethyl iodides with added radioiodine and of methyl iodide in solution in cyclohexane. The wave length used was the 2537 Å mercury line. It was found that the quantum yield of exchange of iodine was near unity, whereas the quantum yield for the formation of iodine was 0.4 for ethyl iodide and 0.016 for methyl iodide, independent of the concentration of iodine in both cases. The authors come to the conclusion that at this wave length there is no primary recombination of iodine atoms and methyl radicals (or ethyl). They assume that the primary effect of the absorption of light is to produce an iodine atom and a high energy radical which then enters into secondary reactions. Such a mechanism will account for different results in different solvents but other mechanisms will also. The principal reason for assuming hot radicals seems to be to get the decomposition yield independent of the concentration of iodine. If the assumed mechanism is correct, the decomposition quantum yield should depend on the concentration of the iodide if the reaction were carried out in an inert solvent. More work needs to be done.

The idea that free radicals may be formed by photoreactions in solution has been given additional support by the work of Evans, Santappa & Uri (24) in which the radicals formed were used to initiate polymerization of vinyl compounds. The photosensitive systems used were the ion complexes of the formula Fe^{+3}X^- in which X^- was chloride, hydroxide, azide. As a result of photoexcitation one of these complexes is converted into a ferrous ion and the corresponding radical. The latter initiates the polymerization of the vinyl compound. The quantum yields for the formation of ferrous ion were found to be 0.05, 0.13, and 0.5 for the hydroxide, chloride, and azide complexes respectively. The amount of polymerization induced depended on the concentration of the monomer but values ranging from 100 to several thousand are listed. A relatively simple reaction scheme is presented which permits the calculation of the relative amounts of polymerization within reasonable limits.

Evans & Uri (25) have discussed the formation of atoms and radicals in solution in another paper with special reference to solutions containing ferric or ceric ions. In the discussion of the chemistry of the ceric solutions they

postulate that hydrogen peroxide may be formed by the action of a hydroxyl radical on a ceric-hydroxide complex. This paper is primarily of a review nature, but it serves to emphasize some of the interesting aspects of this work which has been receiving considerable attention recently.

PHOTOLYSIS REACTIONS

All the net reactions involved in the section on reactions of radicals could be discussed as photolysis reactions since the radicals are formed either in the primary step resulting from the absorption of light or as a result of the collision of a photoactivated molecule with another molecule. However, in those reactions the major interest was in the steps assumed to apply to many reactions, whereas in the systems to be discussed in this section the over-all net reaction is the subject of study although, of course, there is a definite interest in the mechanism required to account for the facts.

Dorfman & Salsburg (26) have studied the decomposition of di-*t*-butyl peroxide over a temperature range from 25 to 75°C. with the full light of the quartz mercury arc and with filters so as to use primarily the light of wave lengths 2537 and 2650 Å. The rates of formation of methane, ethane, acetone, and *t*-butyl alcohol were studied. Methane was found to be of importance only at low light intensities. It is suggested that the primary process is the same as that in the thermal reaction, namely, the rupture of the peroxide bond to form two butoxy radicals. The acetone and ethane are believed to be formed by these radicals losing a methyl group followed by the combination of the methyl groups to form ethane. If this mechanism is correct the ratio of the amount of acetone formed to that of ethane should be two. Experimentally observations were in reasonably good agreement with this hypothesis. The *t*-butyl alcohol can be accounted for by a butoxy radical removing hydrogen from a peroxide molecule. This mechanism requires that if there are no chains, the sum of the quantum yields for acetone and the alcohol should be two. The experimental facts were found to be in accord with this statement at room temperature although an increase with rising temperature was observed which could indicate the existence of short chains at 75°C.

Haynes & Gardner (27) have reported the formation of some methylketene and hydrogen in the photolysis of diethyl ketone at temperatures ranging from 190 to 450°C. The methylketene is believed to be formed by the reaction of an ethyl radical, produced as a result of the light absorption by the ketone, with another molecule of the ketone to form a pentanonyl radical which decomposes into methylketene and another ethyl radical. Other products found are ethane, ethylene, butane, and carbon monoxide. The relative amounts of the various products found are discussed in terms of four possible net reactions, but no numerical values are given to indicate the relative importance of these reactions.

Kandel & Taylor (28) have studied the decomposition of acetic anhydride by the mercury 1850 Å line. The products obtained are approximately equivalent amounts of ethane, carbon monoxide, carbon dioxide with small amounts of biacetyl and methyl acetate. The quantum yield is about two

but increases somewhat as the pressure is decreased. The authors propose a mechanism which involves the formation of an excited molecule which may be deactivated by a collision or decompose by splitting off a methyl radical to form a CH_3COOCO radical, which in turn may split out either carbon monoxide or carbon dioxide to form acetate or acetyl radicals respectively. This mechanism will account for the products and the first order dependence of the rate on the acetic anhydride pressure. Preliminary experiments indicate that the mercury-sensitized reaction yields the same products.

Johnson & Taylor (29) have studied the effect of temperature on the photolysis of methylamine from -15 to 30°C . The effect could be expressed by an activation energy of 6 kcal./mole, but the authors believe that this result may be entirely caused by the change of light absorption with temperature. This possibility was not tested experimentally. It was found that although the disappearance of methylamine is first order the amount of amine decomposed is not measured accurately by hydrogen production, ammonia production, or pressure change. A more detailed study of the products under various conditions is required.

Darwent (30) has studied the mercury-sensitized decomposition of ethylene as the mercury pressure is lowered. He finds that the rate decreases at low pressures of mercury and interprets this result as meaning that the excited ethylene molecules decompose into hydrogen and acetylene only at the surface of the reaction vessel. As the pressure of mercury is reduced, the light absorption occurs deeper in the vessel and as a result the excited molecules have to diffuse farther and have a greater chance of being deactivated without decomposing. He concludes that the average life of an excited ethylene produced by collision with an excited mercury atom is at least 10^{-4} sec.

Caule & Steacie (31) have studied the photolysis of dipropyl mercury at 2500–2700 Å over a temperature range of 30 to 108°C . The principal products are hexane, propane, and propylene and there is no temperature effect. Small amounts of C_2 and C_4 hydrocarbons are also formed.

Ivin & Steacie (32) have studied the disproportionation and combination of ethyl radicals produced in the photolysis of diethyl mercury. The products of the reaction were found to be ethane, ethylene, and butane besides mercury. The temperature was varied up to 200°C . although some thermal decomposition limited the work with low light intensities. It was assumed that the primary effect of the absorption of light was to form ethyl radicals. These reacted according to the equations



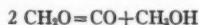
In addition, consideration was given to the possibility of reactions of the radicals with mercury diethyl. Rate laws were derived from the assumed mechanism and it was shown that in the limit of low pressure the two reactions listed above were the determining steps. The difference in activation energy of these two steps, $E_1 - E_2$ was found to 0.8 ± 0.2 kcal./mole. From a

determination of the value of k_2 from experiments using intermittent light, it was estimated that E_2 is not greater than 0.65 kcal./mole. It follows that the dominant reaction at low temperatures tends to be the formation of butane but the disproportionation reaction becomes increasingly important as the temperature is raised. The same conclusion was reached by Comstock & Rollefson (33) on the basis of their studies of the products formed in the action of sodium vapor on ethyl iodide. The amount of butane formation in these experiments was somewhat larger than in Ivin & Steacie's experiments, but this discrepancy may be caused by a catalysis of the recombination reaction by the particles of sodium iodide formed in the experiments. Other data which are at least qualitatively in agreement with these ideas have been presented earlier by Bawn & Tipper (34) for the reaction of sodium with ethyl iodide and by Moore & Taylor (35) for the photolysis of ethyl iodide. Although it seems impossible to carry out experiments so as to be certain that there are no secondary reactions which will influence the results, it does seem quite well established now that the reactions listed above as 1 and 2 occur at comparable rates over a wide range of temperature and that the first increases in importance as the temperature is raised.

Wijnen & Steacie (36) have studied the photolysis of 2,2',4,4' tetra-deuteriodiethylketone. They find that the disproportionation reaction of the ethyl radicals formed yields more than 90 per cent of the ethylene of the formula $C_2H_2D_2$, the corresponding ethane would have to be $C_2H_4D_2$. If the ethyl radical reacts with a ketone molecule the products are ethane and pentanonyl radical. It is estimated that if this reaction occurs with the removal of a deuterium atom from the ketone, the activation energy is 8.7 kcal. but if a hydrogen atom is removed the energy is 11.7 kcal. In other words, the abstraction of a deuterium atom is a faster reaction than that of a hydrogen atom. This is opposite from the usual isotope effect and the difference in activation energies is larger than is usually found in such reactions. Further studies of the isotope effect in such systems should be made. The pentanonyl radical decomposes with an activation energy of about 17 kcal.

REACTIONS OF ALDEHYDES

The past year has brought some additional contributions to the study of the photochemistry of the aldehydes. Calvert & Steacie (37) studied the photolysis of formaldehyde at wave length 3130 Å and at temperatures ranging from 100 to nearly 400°C. They observed a small amount of thermal reaction according to the equation



at temperatures above 150°C. The correction for this thermal reaction never exceeded 10 per cent even at the highest temperatures at which the photolysis was studied. The rate of the thermal reaction was erratic and the temperature coefficient low, facts which suggested to the authors that the reaction is heterogeneous. The results on the photolysis are consistent with

the hypothesis that the primary result of the photoactivation is a rupture of the formaldehyde molecule into a hydrogen atom and a formyl radical. The latter either decomposes into a carbon monoxide and atomic hydrogen or reacts at the wall to form inert products. The former process results in a chain reaction. It was found that propylene and nitric oxide inhibit the reaction, a fact which is in accord with the assumption of a chain process. Some experiments are also reported in which the hydrogen atoms produced by the photodissociation of formaldehyde react with deuterated propane. From the results obtained it is estimated that the difference in the activation energies for the reactions of the atom with propane and with formaldehyde is about 4.5 kcal./mole.

Most of the work which has been done with acetaldehyde during the past year has been concerned with the high temperature photolysis. Danby, Buchanan & Henderson (38) have studied the formation of ethane and hydrogen at temperatures ranging from 200 to 300°C. The analyses were made by means of a mass spectrometer. The proportion of ethane found increased as the temperature was lowered. The discrepancy between this result and that of Blacet, who failed to find ethane at lower temperatures, must depend upon lack of sensitivity in Blacet's (39) experiments or to a different mechanism being predominant at the lower temperatures. One possibility which is mentioned is that the acetyl radical is stable at the lower temperatures as is indicated by the formation of diacetyl. To give validity to this explanation necessitates making the rather reasonable assumption that a methyl radical is much more apt to react with an aldehyde molecule to form methane than it is to react with another methyl to form ethane. Further work by Buchanan (40) was directed towards a determination of the rate of formation of methyl radicals. This was done by adding iodine to the reaction mixture in the hope that it would remove the radicals as fast as they are formed. These experiments showed that the rate of ethane formation at high temperatures was greater than that calculated from the iodine experiments. The discrepancy was attributed to the formation of formyl radicals which decompose at the higher temperatures to give hydrogen atoms which in turn react with acetaldehyde to form hydrogen and methyl radicals. This explanation requires that the formyl radical does not enter into a chain continuing process at the lower temperatures.

Dodd (9) has applied the rotating sector technique of Melville & Burnett (41) to study the effects of intermittent light on the high temperature photolysis of acetaldehyde. From his results he deduces rate constants for the chain propagating and chain terminating steps. They find for the chain propagating step $k = 10^{12.8 \pm 0.4} T^{1/2} \exp(-10.7 \pm 0.5/RT)$ and for the bimolecular chain terminating reaction $k = 10^{13.8 \pm 0.6} T^{1/2} \exp(-0.8 \pm 0.8/RT)$. Dodd suggests that the variations in the activation energy for the chain propagating step which have been reported previously in the literature are caused by a change from a monomolecular chain terminating step at low light intensities to a bimolecular one at high intensities. On the basis of this assumption he sets up an equation with which he corrects the previously reported values

and finds that they agree quite well with the one listed above. He reported that he was unable to decide between the two possibilities $\text{CH}_3 + \text{CH}_3$ and $\text{CH}_3 + \text{CHO}$ as the chain terminating reaction but on the basis of Buchanan's work discussed above it seems that we must conclude that his rate constant is for the reaction of two methyl groups.

Zemany & Burton (42) have sought evidence concerning the relative probability of photoexcited acetaldehyde molecules' breaking into the ultimate molecules methane and carbon monoxide or into a methyl and formyl radical. For this purpose they photolyzed a mixture of ordinary acetaldehyde with the completely deuterated compound. If the rearrangement process is the only one occurring the products should contain only ordinary methane and the completely deuterated compound, but if there is any radical reaction some mixed methanes will also be formed. The products were analyzed by means of a mass spectrograph and it was found that no CH_2D_2 was formed but considerable amounts of CHD_3 were found thus indicating a considerable amount of reaction by the radical mechanism. On the basis of their experimental results and the assumption that the activation energies and frequency factors for the reactions of CD_3 with ordinary and with the deuterated aldehyde are the same, Zemany & Burton calculate the ratio of the radical to the molecular reaction to be 25 at wave lengths greater than 3000 Å and 1.4 with the 2537 Å radiation. Other work (43 to 46) has shown that reactions with deuterated compounds are usually slower than those with compounds containing only ordinary hydrogen. In fact, in another paper Zemany & Burton (47) report that in some studies on the photolysis of acetaldehyde and the D_4 compound at 140°C. the deuterated compound gave a slower rate of photolysis and relatively greater yield of ethane than the ordinary compound. It seems therefore that the ratios given above must be considered as only qualitative although they are in rough agreement with earlier work (48 to 51) which showed that the fraction of the reaction proceeding by the radical mechanism is greater for excitation by long wavelengths than for the excitation by short wavelengths. Zemany & Burton, in this second paper, conclude that in their experiments the radical mechanism accounted for most of the reaction. This is quite possible since at this temperature the quantum yield may be considerably greater than one and it is generally considered that the chain reaction proceeds by a radical mechanism.

Blacet & Calvert (52, 53) have studied the photolysis of butyraldehyde both in the presence and absence of iodine. Both the normal and the *iso* compound were studied and the temperature of the reaction vessel was varied from 25 to 300°C. The products were analyzed by means of a mass spectrometer. The principal products obtained from the normal aldehyde were carbon monoxide, propane, ethylene, *n*-hexane, and acetaldehyde; minor products were hydrogen, methane, and formaldehyde. The quantum yields of carbon monoxide, propane, and hydrogen increase with temperature, while the yields of ethylene and methane are independent of temperature. The products from the isobutyraldehyde were carbon monoxide, pro-

pane, propylene, isopropyl, and as minor products methane and hydrogen. The quantum yields of all the products except methane showed a temperature dependence. When iodine was added to the reacting system, methyl iodide and the appropriate propyl iodide were found. The results can be explained by assuming that as a result of photoactivation some molecules split off either a methyl or a formyl radical but others undergo an intramolecular rearrangement to form the ultimate product molecules. With both aldehydes the direct formation of propane and carbon monoxide is believed to be unimportant at 3130 Å but increases in importance at shorter wave lengths. The direct formation of ethylene and acetaldehyde is important for the *n*-butyraldehyde at all wave lengths. Primary processes leading to the formation of formyl radicals are important for both aldehydes at all wave lengths and the formation of methyl radicals becomes significant for the isocompound at the shorter wavelengths. These results give additional support to the idea which has been in the literature for some time now that the photolyses of molecules of this type proceed both by radical mechanisms and by the direct formation of product molecules.

REACTIONS OF THE HALOGENS

Three papers by Van Artsdalen and co-workers (54, 55, 56) have discussed the bromination of toluene and neopentane. Both are chain reactions in which a bromine atom is believed to react with the hydrocarbon to form a radical and hydrogen bromide; the radical then reacts with a bromine molecule to form a bromide molecule and a bromine atom. The reactions are therefore entirely analogous to the photoreactions of bromine with hydrogen or methane. Only preliminary results are given for toluene but the neopentane reaction is discussed in detail. For the latter reaction the authors report the activation energy for the step involving a bromine atom and neopentane molecule to be 18.1 kcal./mole and the steric factor to be 473. They ascribe the latter value to a "chain reaction of some length." This explanation is not in accord with their mechanism since only one molecule of product is formed for each time this step occurs. It is more likely that the activation energy used in calculating this steric factor is in error because of failure to allow for the change in absorption of light by the bromine as the temperature was changed in the photochemical reaction.

From a comparison of the thermal and photochemical rates of bromination of neopentane and hydrogen, Schweitzer & Van Artsdalen conclude that the former substance is 174 times as effective in bringing about the recombination of bromine atoms as in hydrogen. For this calculation they use their own values for the rates of the photobromination reactions but take the thermal rates from two different researches. This procedure introduces some uncertainty into the quantitative aspects of the calculation but it seems reasonable that the more complex molecule should be considerably more efficient for such a process.

Hormats & Van Artsdalen use their calculated activation energies to estimate the C—H bond strength in neopentane. Their figure of 96 kcal./mole

at 400°K. is a little lower than the values ordinarily accepted for methane and ethane, but it seems reasonable.

Jones (57) has studied the relative rates of reaction of hydrogen and tritium hydride with chlorine using both light and beta particles as the means of excitation. The ratio of the rates is expressed by $R = (1.35 \pm 0.03) \exp((552 \pm 7)/RT)$ to within about 0.3 per cent. The ratio is not dependent on the method of excitation. The results are discussed in terms of the absolute rate theory, but with any of the models assumed for the activated complex there is a considerable discrepancy between the experimental and calculated results.

Winning (58) has studied the photochlorination of chloroform over a wide range of conditions and finds that the rate can be expressed by $d(\text{CCl}_4)/dt = (a(\text{CHCl}_3)(\text{Cl}_2)(I_{\text{abs}}))^{1/2} / ((\text{CHCl}_3) + b)^{1/2}$ in which a and b are functions of the rate constants for the steps in the assumed mechanism which proceeds through the formation of CCl_3 radicals. This law reduces to the same form as found by Schumacher & Wolff (59) for high chloroform concentrations. Winning assumed that the chain terminating step is a trimolecular reaction between two CCl_3 radicals and a chlorine molecule to form carbon tetrachloride rather than the formation of hexachloroethane. He had no evidence against the formation of the latter compound; it was merely a case of not observing it. In view of the positive identification of hexachlorethane as a product by Newton & Rollefson (46), the formation of this compound seems to be a more logical chain terminating step to assume although the actual choice is not of great importance in determining the rate law.

Ketelaar *et al.* (60) have studied the reactions between bromine and 1,2 dichloroethylene. Both the isomerization and the addition reactions were studied. The absolute rates showed considerable variation because of various unknown factors which influenced the chain length but the ratio of the two processes is essentially unaffected by these disturbing influences. The results obtained are consistent with a mechanism in which a bromine atom reacts with a dichloroethylene molecule to form a radical ABr , which may then react with bromine to form the addition product or it may dissociate to form either the original substances or the isomer of the ethylene. The essential features of the mechanism have been in the literature for many years.

Rutenberg & Taube (61) have continued their work on the efficiency of the primary photochemical process for halogens in water with a study of the reaction between Mn(II) and bromine with a few supplementary experiments using iodine. Since the quantum yield of the reaction is independent of the manganese concentration, they conclude that the measured yield is that of the primary process. The yield depends on whether Br_2 , Br_2^- , or Br_2Cl^- is the absorbing substance; the observed values at 4360 Å and 19°C. are 0.043, 0.122, and 0.142 respectively. These yields increase with temperature, energy of the quantum, and, in the case of tribromide, with the concentration of the bromide ion. The authors discuss their results at some length, and with the aid of *ad hoc* assumptions they give a partial explanation of the observed effects. If the ideas expressed are correct, the same variations in

efficiency should be found in systems containing other reducing agents. Such work has not been done as yet.

SENSITIZED REACTIONS

The past year has seen the continuation of the studies of mercury-sensitized reactions by Steacie and his collaborators (62 to 66). In all of these, reactions between the photoactivated mercury atom and the molecule under investigation lead to the formation of a radical so that essentially these papers deal with the reactions of radicals. The decompositions of ethane (66) and propane (65) were studied at high temperatures and it was found that the ethyl and propyl radicals are unstable above 400 and 450°C. respectively. The propyl radical gives ethylene or propylene with activation energies of 20 and 38 kcal. respectively. The activation energy for the decomposition of ethyl into ethylene and a hydrogen atom is given as 39.5 kcal. The reactions of butyl and isobutyl are somewhat more complex. With benzene the maximum quantum yield was found at 400°C.

Schenck (67, 68, 69) has studied the reactions of a number of organic substances with O_2 for which fluorescent dyestuffs act as sensitizers. The general scheme he proposes for the mechanisms of these reactions is as follows: (a) The sensitizer absorbs light and goes into a diradical or triplet state. (b) This excited state may be deactivated by the acceptor (k_{IV}), or it may react with oxygen to form a reactive addition compound (k_{II}). (c) This addition compound may decompose to form the normal sensitizer and oxygen (k_V), or it may react with the acceptor to form a peroxide and the normal sensitizer (k_{III}). These assumptions lead to the equation

$$d(AO_2)/dt = \frac{I(A)}{1 + k_{IV}(A)/k_{II}(O_2) + k_V/k_{III}}$$

for the formation of the peroxide. In this expression I represents the rate of light absorption and (A) , (O_2) , and (AO_2) the concentrations of the acceptor, oxygen, and product respectively. Many examples of the sensitized oxidation of unsaturated organic molecules are shown to be in accord with this scheme. The relative rates of the assumed steps vary from one system to another, but there can be little doubt that mechanisms of this type are of wide applicability.

OTHER REACTIONS

Davidson *et al.* (70) have used the intense flashes of light of the type described by Porter & Norrish (12) to produce iodine atoms and study the rate of recombination. They found the average value of the termolecular rate constant with argon as the third body to be 4.5×10^9 compared to the value of 6.5×10^9 found by Rabinowitch & Wood (71).

The quenching of fluorescence has been used as a means of studying reactions. During the past year Rowell & LaMer (72) have published some results on the quenching of uranin by a number of organic nitrogen compounds. A considerable variation in the efficiency was found. It was found

that this variation was not associated with the basicity of the nitrogen but could be correlated with resonance effects which influence the ease of losing an electron. If this explanation is correct, the relative efficiencies of these substances in quenching other fluorescers should be the same although the absolute magnitudes may be quite different. It is unfortunate that at least one other substance was not tried.

Volman (73) has studied the reaction between ozone and hydrogen peroxide using the 2537 line of mercury for excitation. Although both substances absorb light of this wave length, the absorption by ozone is so much stronger than that by hydrogen peroxide that it is assumed that only the former need be considered. The quantum yield is well under one but is several times as large in a mixture of the gases as it is in pure ozone. A mechanism involving activated ozone molecule, oxygen atoms, HO and HO₂ radicals is presented.

Burton *et al.* (74, 75, 76) have compared the photochemistry and radiation chemistry of a number of alkyl-substituted benzenes. The quantum yields are all low, of the order of 10^{-4} . The results are discussed in terms of carbon-carbon split, usually β to the ring, to form methyl radicals. The major interest in these papers is in their radiation chemistry.

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PHOTOSYNTHESIS^{1,2}

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Although there has been considerable progress toward an understanding of the processes of photosynthesis in recent years, the advances have been followed rather closely by symposia, monographs, and reviews of the subject matter, particularly during the last three years (1 to 8).⁵

In view of the comprehensive coverage it would appear that the present review might very well be limited to a discussion of certain subjects of special interest to the authors and some with which they are especially familiar. These are the extensive discussion by Warburg and his co-workers of their proposal for the existence of a light induced oxygen absorption (and corresponding carbon dioxide evolution) which can amount to three or four times the net oxygen evolution by the same light; and the discovery of the early participation of seven and five carbon sugars in carbon dioxide reduction in photosynthesis together with some observations on the kinetics of the metabolic transformations.

While it is true that a considerable number of significant publications have appeared in other aspects of photosynthesis [the Hill reaction and its coupling with carbon dioxide reduction (9 to 19); photochemistry of chlorophyll and related synthetic materials as model reactions in relatively simple defined physical systems (20 to 23); transfer of light energy within the pigment systems (24, 25)], it is felt that they represent confirmation and extension of ideas which have already been discussed in a variety of earlier reviews and that a re-evaluation of them might very well be postponed until a later time.

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⁴ Fellowship of the Swiss Foundation: "Stiftung für Stipendien auf dem Gebiete der Chemie."

⁵ Reference 7 refers to the Conference on the Sun in the Service of Man, February 24-25, 1951, and contains the general discussions of the possible application of photosynthesis and knowledge about photosynthesis rather than detailed information about its mechanism. Reference 8 admits to conferences as late as March, 1951, but actually discusses much information which was not published at that time.

THE ONE-QUANTUM PROCESS

In the course of studies on the maximum possible obtainable efficiency of photosynthesis, Warburg and his associates, using the gas exchange method that commonly bears his name, had occasion to shorten the alternating light and dark periods, between which the net gain of oxygen or loss of carbon dioxide is determined, to intervals of one minute of illumination alternating with one minute of darkness. Under these circumstances, the apparent efficiency of oxygen production during the one minute illumination rose to a value which, when expressed in terms of the number of molecules of oxygen produced per quantum of light absorbed, approached one (26, 27, 28). At the same time, the apparent gas absorption in the one minute dark interval increased to values of the order of ten times that normally observed for dark respiration over long periods of time. This enhanced oxygen absorption observed immediately following the illumination period is supposed to be going on during the illumination as well, thus leading to the suggestion that at all times under these optimum conditions, oxygen is actually being produced at a rate corresponding to one mole per quantum absorbed but that two-thirds to three-fourths of this oxygen produced is re-absorbed in a light-enhanced back reaction leaving the net oxygen production observable for long periods corresponding to an efficiency of the order of one-fourth molecule of oxygen per quantum absorbed. All the above observations, which refer to molecules of oxygen evolved in the light and absorbed in the dark, are supposed to be pertinent as well to molecules of carbon dioxide absorbed in the light and evolved in the dark.⁶

In later publications (34, 35), Warburg was able to observe the gas exchanges immediately following the application of the measured light and immediately following the cessation of the measured illumination and to plot these changes as a function of time, making observations at one minute intervals. A typical result is shown in Figure 1 (35). In this experiment, the unmeasured white light is applied so as to just balance the oxygen evolution and the carbon dioxide absorption by photosynthesis with the carbon dioxide

⁶ Practically all of these observations were made by the "two-vessel" method, a relatively new description of which is to be found in the papers by Warburg & Burk (29) and Burk, Schade, Hunter & Warburg (30). Since most of the observations were on *Chlorella*, the physiological pH range of which is of the order of 4.5, the actual pressure changes observed when the experiments are performed in this pH range are a result of the difference in solubility in the medium between oxygen and carbon dioxide. By using a pair of vessels whose geometry with respect to the algae and light are identical except for the gas volume above the algae suspensions, it becomes possible to determine, on the comparison of the observed pressure changes in the two different vessels, the ratio of oxygen over carbon dioxide whether it be in light or dark. Having determined this, the observed pressure change in a single vessel can then be converted into moles of oxygen evolved (absorbed) and moles of carbon dioxide absorbed (evolved). It should be pointed out here that there is a real difference of opinion as to the validity of the observations made by this method, and these questions have been listed and discussed at some length (31, 32, 33).

evolution and oxygen absorption by respiration so that the manometers show no changes in pressures with time. Pressure changes are then brought about by the additional illumination with a measured beam of green light. Taking the data at face value, it is evident that what is represented in Fig-

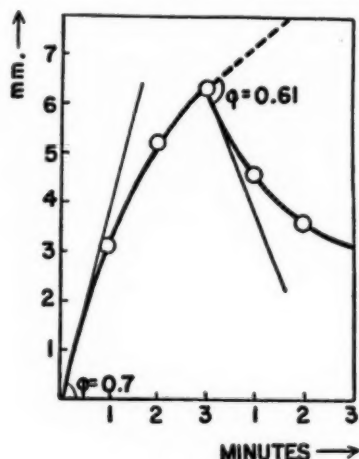


FIG. 1. Division of photosynthesis into light reaction and back reaction. One hundred cubic millimeters of wet packed cells (*Chlorella*) are suspended in 7 ml. water at a temperature of 20°C., a light intensity of measured light equal to 17.3 mm.² quanta/min. or 2.8×10^{-3} watts at 546 m μ and a partial pressure of carbon dioxide equal to 0.109 atm.

ure 1 is a transient phenomenon with a logarithmic approach to a steady state. Warburg has chosen to interpret this result in terms of a primary photochemical reaction yielding molecular oxygen with a quantum requirement of one, accompanied by the proportional generation of a substance c (substances) which reacts with a fraction ϵ of the generated molecular oxygen, with a specific reaction velocity k . In qualitative terms, then, the falling off of the increase in pressure curve (Fig. 1) is supposed to be due to the building up of the back reaction substance c . This he has expressed in algebraic terms in the following way:

Let

I_a = absorbed light intensity per minute, expressed as mm.² quanta/min. unit vol.

t = time of illumination by the measured light (min.)

x = evolved O₂ in time t by light I_a , in mm.³ O₂/unit vol.

ϵ = the fraction of the O₂ evolved by the light reaction which reacts back.

c = concentration of the substance controlling the reverse reaction expressed in terms of back-reacting O₂ as mm.³ O₂/unit vol.

k = specific rate constant of the back reaction (min.⁻¹)

If the light intensities are so adjusted that the quantum requirement for O_2 in the light reaction, ϕ , is 1 then (since $I_a = +dO_2$ (light reaction)/ dt) then

$$+dc/dt = \epsilon I_a - kc \quad 1.$$

integrated

$$\begin{aligned} dc/(\epsilon I_a - kc) &= dt \\ -1/k \ln (\epsilon I_a - kc) &= t + \text{const.} \end{aligned}$$

When

$$\begin{aligned} t=0 \quad c=0 \quad \text{Const.} &= -1/k \ln \epsilon I_a \\ \ln [\epsilon I_a/(\epsilon I_a - kc)] &= kt \\ \epsilon I_a &= e^{kt}(\epsilon I_a - kc) \\ \epsilon I_a e^{-kt} &= \epsilon I_a - kc \\ c &= \epsilon I_a(1 - e^{-kt})/k. \end{aligned}$$

When

$$t \gg 1/k \quad c_{\text{station}} = \epsilon I_a/k.$$

Further (if $\phi=1$)

$$dx/dt = I_a - kc. \quad 3.$$

Substituting 2 into 3 to eliminate c

$$dx/dt = I_a - \epsilon I_a(1 - e^{-kt}) \quad 4.$$

With the boundary conditions

$$\begin{aligned} t=0, \quad dx/dt &= I_a \\ t \gg 1/k, \quad dx/dt &= I_a(1 - \epsilon). \end{aligned}$$

Equation 4 gives on integration

$$x = I_a(1 - \epsilon)t + \epsilon I_a(1 - e^{-kt})/k \quad 5.$$

with the boundary conditions

$$t=0, \quad x=0 \text{ giving } t \gg 1/k, \quad x = I_a(1 - \epsilon)t + \epsilon I_a/k$$

If the quantum requirement is explicitly retained

$$x = I_a\phi(1 - \epsilon)t + \epsilon\phi I_a(1 - e^{-kt})/k. \quad 6.$$

It is thus clear that the initial slope of the oxygen evolution curve should represent, according to this picture, the quantum requirement of the primary photochemical oxygen evolution, while the initial slope of the absorption curve following the cessation of illumination should correspond to the quantum requirement of the continuous production of the back-reacting substance c . This latter, by the definition of c , should be equal to the former. There is some question as to the general validity of the observation itself (31, 32, 33), and this is especially true where very rapid observations are necessary. The question immediately arises as to how nearly the components of the gas phase are in equilibrium with the gaseous components of the solution and with the gaseous components within the green cells themselves. It

is clear that if oxygen comes to equilibrium in these systems somewhat more rapidly than does carbon dioxide, a result such as that given in Figure 1 would ensue. Furthermore, this difference in rate might occur in the transfer between the gas phase and the liquid medium or between the liquid medium and the green cell interior where presumably the gases are ultimately generated or absorbed.

However, even accepting the existence of this transient approach to a steady state associated with a change in light intensity as significant for the chemistry of the green cell itself, the interpretation given by Warburg is not unique but only one of a number of possible views even on a quantitative basis. The striking similarity between the data presented and the transient appearing in the electrical circuits cannot be overlooked. In fact there has been evidence for oscillatory transients in both carbon dioxide and oxygen evolution as well as fluorescence reported repeatedly, the most recent of which is that of Van der Veen (36). One of the simplest of such circuits would be a parallel arrangement of a resistance and a capacitor-resistance. The change in light intensity would correspond to a change in impressed potential, and the gas flow would correspond to the charge flow. In chemical terms, the resistance would correspond to the specific rate constants of a series of reactions, while the capacitance would correspond to the size of the reservoirs involved in the equilibrium, which was shifted and maintained by a change in the steady state. It might be worthwhile to actually outline one such case in as general terms as possible.

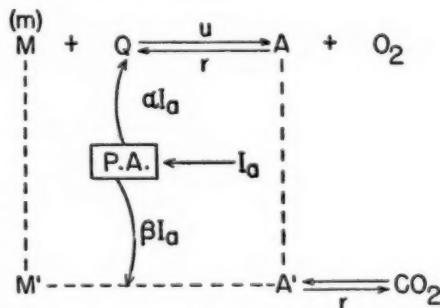


FIG. 2

A likely system having some of the above elements is shown diagrammatically in Figure 2 where the equilibrium between M and A + O₂ would correspond to the terminal oxygen evolving reaction. Defining corresponding terms in units similar to those used in the preceding derivation let

I_a be the amount of light (number of quanta) absorbed by the photochemical apparatus (represented by the box P.A.) where it is converted into some chemical form (reduced and oxidized species).

α be the proportionality constant between the number of quanta ab-

sorbed and the number of molecules (Q) of some species which reacts with the species M to produce molecular oxygen with a rate constant of unity ($u = 1$).

r be the constant rate of the reverse reaction in the final equilibrium with molecular oxygen (also with carbon dioxide).

β be the proportionality constant between the number of quanta absorbed and the steady net rate of formation of M .

m be the concentration of M at time t .

x be the number of moles of oxygen produced in time t .

Then,

$$dx/dt = (\alpha I_a)m - r \quad 7.$$

and

$$dm/dt = -\alpha I_a m + \beta I_a + r. \quad 8.$$

Substitute p for $\beta I_a + r$

and q for αI_a

to give

$$dx/dt = qm - r \quad 9.$$

$$dm/dt = p - qm. \quad 10.$$

Integrate equation 10 with the limiting condition $m = m_0$, when $t = 0$, to give

$$m = p/q + (m_0 - p/q)e^{-qt}. \quad 11.$$

Substitute equation 11 into equation 9 and integrate with the limiting condition that $x = 0$ when $t = 0$, gives

$$x = (p - r)t + (qm_0 - p)(1 - e^{-qt})/q \quad 12.$$

or replacing p and q ,

$$x = \beta I_a t + [\alpha I_a m_0 - \beta I_a - r(1 - e^{-\alpha I_a t})]/\alpha I_a. \quad 13.$$

Equation 12 (equation 13) gives precisely the same relationship between the amount of oxygen evolved and time as does equation 5 (equation 6), the difference being in the significance of the constants.

It is thus apparent that the existence of a light-induced reaction consisting in the absorption of molecular oxygen and the evolution of molecular carbon dioxide at a rate of approximately three times that of the net evolution of oxygen induced by the same light is not an inescapable conclusion to be drawn from the data as presented by Warburg. In fact, there exist two pieces of independent experimental evidence which would seem actually to preclude such a possibility. The system of forward and reverse reactions as proposed by Warburg is represented in its simplest form in Figure 3.

Thus, for every four molecules of molecular oxygen which are produced by the photochemical reaction, three are supposed to be reabsorbed by the photosynthetic system in a dark reaction. Similarly, for every four molecules of carbon dioxide which are absorbed in the photochemical reaction, three are re-evolved in this same dark reaction. Since the photochemical reaction

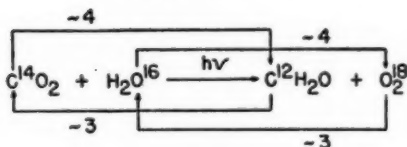


FIG. 3

is supposed to have a quantum requirement of unity, it is clear that the quantum requirement for the net production of molecules of oxygen will be approximately four. Such a system would lead to a very rapid exchange between the oxygen atoms of the gaseous molecular oxygen and those contained in combination with the living organism as water and in other combined forms. The same accelerated exchange would be expected between the carbon atoms of the gaseous carbon dioxide and those incorporated in the photosynthetic organisms. The number of molecules exchanged (oxygen or carbon dioxide) resulting from this type of reaction alone should be approximately three times the net number of oxygen molecules produced. It is possible to determine whether or not such photochemically accelerated exchanges take place and, in fact, both of these isotopic tests have been applied, although not on the same systems.

Thus, if the organism is placed in contact with gaseous molecular oxygen labeled with O^{18} and the rate of change of the specific isotopic content of the gas is determined in the dark and compared with that which occurs upon illumination, it should be possible to detect an accelerated rate of disappearance of labeled oxygen from the gas phase, since any labeled oxygen atom which is recombined in the organism will be so diluted by the large amount of unlabeled oxygen in the organism that it will not reappear in the gas phase. In effect, this means that photochemically produced oxygen would have no label whereas that which is being reabsorbed would, of course, have the label from the gaseous phase. Experiments of this sort have been done by Brown, Nier & Van Norman (37) on a variety of organisms including *Chlorella*. In no case was there any evidence of an increased rate of disappearance of O^{18} from the gas phase under the influence of light.

The corresponding experiment with labeled carbon dioxide using C^{14} -labeled CO_2 has been done by Weigl & Calvin (38) on barley leaves. Here, also, there is no evidence of accelerated dilution of the residual carbon dioxide with non-labeled carbon from the organism under the influence of light. In fact, the only effects reported in each case were inhibitory effects on both of the rates mentioned.

The conclusions which were drawn by the authors of each of these above-mentioned experiments were weakened by the suggestion that upon illumination the oxygen which is absorbed in the respiratory reaction does not escape from the cells after its photosynthetic production, and the carbon dioxide evolved in the respiratory, or "back," reaction does not escape from the cells prior to its photosynthetic incorporation. This criticism is incom-

patible with the assumption that the curves in Figure 1 are significant. In order that these curves, which are manometric changes with time, should correspond to the rates of chemical processes within the photosynthetic organisms, it was necessary to assume a complete equilibration between the gas phase and the molecular oxygen and carbon dioxide within the cell wall.

It thus appears that the transient phenomena observed by Warburg are better accounted for in terms of shifts of equilibria or steady states rather than in terms of an increased back reaction from the gas phase.⁷ It is also clear that under some circumstances it should be possible to observe, for short periods of time, rates of oxygen evolution or carbon dioxide absorption which would correspond to the apparent quantum requirements, even less than one (apparent quantum yield greater than unity). This is in no way to be construed as a violation of the Einstein law of photochemical equivalence. Without doubt there is a primary photochemical act somewhere in the photosynthetic apparatus which involves the transformation of electromagnetic to chemical energy with a quantum requirement of one, i.e., for every quantum absorbed one photochemical equivalent of a reaction will be brought about with concomitant storage of chemical energy. There is, of course, no requirement that there be any unitary relationship between quanta and molecules of gas observed manometrically.

This implied relationship between the number of quanta which might be required in the over-all energy balance for the production of oxygen, the absorption of carbon dioxide, and the mechanism by which this is achieved has led very often in the past thirty years to attempts to find ways of storing electromagnetic energy in that form, since it was clear very early that the amount of energy required to achieve the over-all reaction of photosynthesis corresponded to that contained in at least four quanta. With the growth of our knowledge of the way in which biochemical systems manipulate and convert energy from one form into another, e.g., the conversion of chemical energy to mechanical energy in muscle, has come the realization that the accumulation of the necessary calories to perform the over-all reaction of photosynthesis might be done better chemically. It would appear that this is the predominant conception at present as it has been expressed in a wide variety of ways by many authors in many places. It would be futile at this point to try to review the history of the development of this idea in all its ramifications (5). Among the first of such suggestions was that of Ruben (39) and also of Lipmann (40) that energy required to carry out the over-all photosynthetic reaction might be transported, at least in part, through high energy phosphate. This has even been carried to the extreme with the suggestion that there might be a 1:1 correspondence between quanta absorbed and individual high energy phosphate bonds formed, e.g., the terminal phosphate

⁷ This includes the possibility that they will be the result of differences in the specific rates of passage of oxygen and carbon dioxide through the cell wall. It is, however, unlikely that differences in the rate of establishment of equilibria between the medium and the gas can be called upon to account for it, as independent experiments in the authors' laboratory confirm.

bond of ATP. This idea has been criticized on the basis of its enormous inefficiency (approximately 40 kcal. quanta being used to produce a single 12 kcal. bond) and almost certainly rightly so. The other alternative, namely, the subdivision of a quanta into two or three parts, has been rejected on the basis of lack of precedent (41). This is, however, probably due to the explicit or implicit attempt to perform the subdivision while the energy is in electromagnetic form or in the form of electronic excitation. This difficulty disappears if the conversion to chemical energy takes place at the 40 kcal. level, or thereabouts, and its subdivision occurs thereafter.

In relatively recent years a number of proposals have appeared concerning some of the more or less specific methods by which energy might be converted and brought to bear upon the oxygen liberation reactions and the carbon dioxide reduction reactions. With the confirmation (42, 43, 44) of the idea that the reduction of carbon dioxide was separable^{*} from the primary photochemical act and was in itself a completely dark reaction (44) and the discovery that the earliest isolable intermediate of carbon dioxide incorporation by photosynthesis was phosphoglyceric acid, it became possible to suggest specific patterns by which high energy phosphate might play a part. It was clear that the initial carboxylation reaction leading to phosphoglyceric acid required the presence of a phosphorylated intermediate of relatively high energy level. This was presumed to have been formed either directly or indirectly through some oxidation reaction (not necessarily involving oxygen directly).

It was therefore proposed (47) that part of the initially produced reduced carbon be passed through a reoxidation cycle and thus have some of the reduced energy originating from the light reaction converted into high energy phosphate. The passage of an electron from a high reducing potential to a lower one on its way to molecular oxygen produces high energy phosphate. Evidence that such reactions might play a part in photosynthesis has been recently added to the literature (48).

These, and many other such suggestions, are all part of the same general conception of the rearrangement of chemical energy in dark reactions in preparation for the two reactions which can be observed manometrically in photosynthesis, viz., the evolution of molecular oxygen and the absorption of molecular carbon dioxide. It is in the reiteration and emphasis of these ideas that the importance of the recent Warburg publications seems to lie, irrespective of whether or not the one quantum process has been observed manometrically, or even whether it will ever be.

Such a relation between dark reactions involving the accumulation and redistribution of energy and the gas exchange observable as a result of photo-

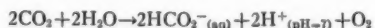
^{*} During the past year there has been discovered what appears to be a chemical light production following illumination of green plants (45) and also of isolated chloroplasts (46). This has a lifetime of the same order of magnitude as the "stored reducing powers" (43) and is quenched by carbon dioxide in much the same way. Therefore it seems that at least part of the initial path of entry and conversion of the photon is reversible.

chemical processes would necessarily have to be considered in any determination of the over-all efficiency of the green plants in the energy conversion process, particularly when this determination is made via a gas exchange measurement. The efficiency of the energy conversion on the basis of the amount of carbon dioxide incorporated must depend very sharply on the fate of the carbon dioxide, since the energy required to reduce carbon dioxide to the level of formic acid is considerably less than that required to reduce it to the level of formaldehyde and this, in turn, is less than that required to reduce it to the level of methanol. On the other hand, the energy required to produce a mole of oxygen from water is very nearly independent of the fate of the hydrogen atoms involved in the reaction and is approximately 115 kcal.⁹ Therefore, measurement of oxygen evolved provides the preferable manometric unit for the determination of the efficiency of energy conversion.

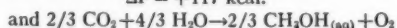
However, the source of the energy required for this oxygen evolution might not be the immediately absorbed and measured light entirely. If some fraction of the energy transformed in the respiratory reactions were used in preparing intermediates for the oxygen evolution reaction, it is clear that this respiratory energy (measured by the amount of oxygen absorbed in the dark period) should not be subtracted from the observed oxygen evolution in a light period for the determination of an efficiency. If the measured light is of such intensity and under such conditions as to merely decrease the rate of oxygen absorbed, the actual rate of energy transformation into a chemical form is still negative; that is, no energy is being stored but rather it is being expended. If we try to use the difference between the rate of oxygen absorption in the dark and the smaller rate of absorption in the light as the rate of energy storage due to the light itself, the result might very well be completely erroneous. Some unknown fraction of the energy being expended might actually be in the course of transformation and utilization for the preparation of compounds (intermediates) making it possible to evolve molecular oxygen from them by the addition of some energy directly from the measured light absorbed. Even if the light intensities and conditions are such as to lead to an actual evolution of oxygen, it would still be an error to subtract from that evolution the apparent amount of oxygen absorbed in the dark either just before or just after the illumination period. This would be true irrespective of whether this so-called dark respiration is affected by light or not; that is, whether the dark respiration, as observed just prior to, or just succeeding an illumination period, proceeds at exactly the same rate or at some changed rate during the illumination period.

If it proceeds at the same rate, then the energy so generated, or some fraction of it, may be used to prepare intermediates for oxygen evolution. If there is an intrinsic inhibition or acceleration of this process by light, then this same energy is being stored. Since the fraction of this respiration gener-

⁹ For example



$$\Delta F = +117 \text{ kcal.}$$



$$\Delta F = +110 \text{ kcal.}$$

ated energy which may contribute to oxygen evolution is not known and may approach unity, it thus becomes impossible to determine accurately the efficiency of the energy conversion process from a gas exchange experiment alone when the net oxygen evolution is not very large as compared to the dark respiration. The possible error from this source is, of course, that percentage of the total oxygen evolution which corresponds to the respiratory oxygen adsorbed.

When the efficiency is determined by differential addition of light and measurement of the corresponding additional oxygen evolution, even if the initial state is one in which there is no net oxygen absorption (due to compensating light), this possible contribution of respiratory energy to the oxygen evolution reaction has not been considered or corrected for. The fraction of the energy from the compensating light which may be co-operating in the oxygen evolution almost certainly is dependent upon the differentially added light. The experimental result consequent upon this argument seems to have been observed by Kok (49). In these observations the value of $\Delta[(dO_2/dt)]/\Delta I$ is dependent upon the value of I particularly at intensities around the compensation point.¹⁰

CARBON METABOLISM

In the course of studies designed to give more specific information about the sequence of compounds involved in the incorporation of carbon dioxide into plant substances, two new early products of this incorporation have been uncovered. These are certain phosphates of the seven and five carbon sugars, sedoheptulose and ribulose, respectively (50 to 53). An examination of the kinetics of their appearance together with a number of other compounds in what is purported to be a steady state photosynthetic system has been made (54). Their appearance in the first few seconds of photosynthesis, the lack of any configurational relationship between them and the usual ultimate products, hexoses (glucose, fructose and sucrose), together with preliminary information suggests that the labeled carbon atoms appear somewhere in the very rapidly turning cycle for the regeneration of the two-carbon dioxide acceptor which ultimately leads to phosphoglyceric acid. This relationship is illustrated in Figure 4.

Ample precedent already exists for the fission of a ketopentose, such as ribulose, between carbon atoms two and three, giving a two-carbon fragment and a three-carbon fragment (55, 56). In a similar manner, 2-ketoheptoses, such as sedoheptulose, would yield a two-carbon fragment (possible phosphoglycolal) and a five-carbon fragment leading to the ketopentose. The question of the source of the seven-carbon heptose must then be answered. The rather obvious possibility of its formation by the condensation of a four- and three-carbon piece presents itself, and we are again faced with the problem of the character and identification of the four-carbon fragment which would be involved. The problem of the identification and character of this four-carbon

¹⁰ At very high light intensities the value (efficiency) falls off because of other limitations upon the rate of energy utilization.

$$\Delta F = +117 \text{ kcal.}$$

$$\text{and } 2/3 \text{ CO}_2 + 4/3 \text{ H}_2\text{O} \rightarrow 2/3 \text{ CH}_3\text{OH}_{(\text{aq})} + \text{O}_2$$

$$\Delta F = +110 \text{ kcal.}$$

fragment among the early products of steady state photosynthesis still remains as it did in all earlier schemes.

However, there is indication from paper chromatography of the presence of a phosphorylated erythronic acid among early products of photosynthesis. Since this compound is never present in very large concentrations, at least under the conditions we have so far used for examination, it would indicate a very small steady state reservoir of this compound. This is true also of the corresponding sugar phosphate, viz., phosphoerythrose, which is thought to react with triose phosphate to give a sedoheptulose phosphate. It should be pointed out that in the regeneration of the two-carbon unit it is possible to bypass entirely the need for either four- or seven-carbon units as well as a second carboxylation reaction.¹¹ This is done by using the recently revived (58, 59) route of Dickens (60) from glucose to ribulose via 3-keto gluconic acid and a decarboxylation. However, there would be no net gain in reduced carbon in such a cycle and other ports of carbon dioxide entry would have to be provided.

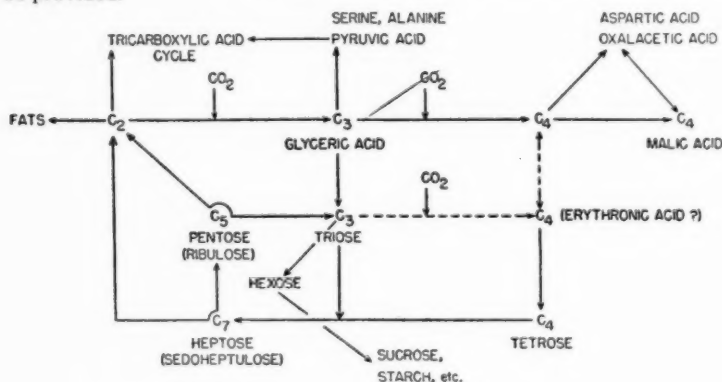
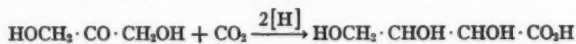


FIG. 4

The dotted arrow leading directly from triose to erythronic acid would correspond to the reductive carboxylation of dihydroxyacetone



which is exactly analogous to the reductive β -carboxylation of pyruvic acid leading to malic acid. The existence of enzymes capable of performing the latter reaction has been demonstrated. Figure 4, of course, is designed to represent only the transformations occurring in the carbon skeleton. It awaits further definition by more extensive kinetic studies as well as isolations and degradations which are yet to be performed.

It is interesting to note and specifically point out here the further development of the basic idea of a very close interweaving of the wide variety

¹¹ The desirability of avoiding the second carboxylation reaction in photosynthesis was suggested by Gaffron and his co-workers some years ago (57).

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of metabolic reactions, some of which might be conceived as being primarily associated with photosynthesis while others are usually, or more often, associated with respiratory and other biosynthetic transformations. It is clear, for example, how it might be possible for the products of carbon reduction formed in the closed cycle, shown above, to enter into the tricarboxylic acid cycle and thus produce high energy phosphate by already known mechanisms. It should be remembered that not shown in Figure 4 are the compounds giving the reducing power which would be required to drive such a cycle and which have their primary origin in the photochemical apparatus. It is also clear that a change in the rate of any one of the reactions shown would affect the stationary state concentrations of almost every compound shown there.

It is the development of such a conception as this, not only for the carbon dioxide cycle but for the oxygen evolution cycle as well, in specific chemical terms, which we feel sure will ultimately lead to the clear understanding of the enormous variety of observations on photosynthetic organisms and systems in general which have been reported since the character of the phenomenon was first recognized.

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SPECTROSCOPY

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This review surveys the main avenues of progress in spectroscopy, with the exception of microwave spectroscopy, during the year 1951. The literature of previous years has not been examined systematically although some references to earlier work have necessarily been included. Owing to the reviewer's geographical location, it has not been possible in general to mention journals that appeared later than October 1951. There seem to have been no major developments during the year, but rather there has been steady progress on a wide front. Limitations of space render it impossible to make reference to all the interesting work that has appeared in the various fields of spectroscopy, but it is hoped that a balanced impression has been given. During the year there appeared in published form a valuable summary of spectroscopic work that is contained in the Faraday Society Discussion (1) on spectroscopy and molecular structure, including electronic, vibrational, and rotational spectra, the vibrational spectra of complex molecules, and a number of important papers on optical methods of investigating the structure of the living cell.

In the present review we begin with current aspects of vibration-rotation spectra, followed by a survey of electronic spectra, particularly for organic molecules. In the concluding pages some attention is given to those rather less tangible and less carefully studied phenomena concerned with the spectroscopy of molecules in the close environment of other molecules. The topics surveyed at this stage include some reference to the effect of solvents on spectra and also to cases where the appearance of intense absorption seems to depend on the interaction of particular molecular species that are present together in the same solution.

VIBRATION-ROTATION SPECTRA

Theoretical.—Amongst the year's theoretical studies, first mention should be given to Nielsen's (2) comprehensive review on molecular vibration-rotation energies. Crawford & Fletcher (3) have reported on the matrix method of determining normal co-ordinates. The problem of including the van der Waals' forces between nonbonded atoms in molecular potential energy functions was given a general treatment by Torkington (4). The vibrations of ethylene and of substituted ethylenes were dealt with in two papers by Torkington. In the first (5), he reanalysed the planar vibrations of C_2H_4 and C_2D_4 and evaluated the $C=C$ stretching constant. In the second (6), the normal co-ordinates of a series of substituted ethylenes were treated with particular reference to the nonplanar vibrations of $=CH_2$. He found

that the =CH_2 bending constant was decreased by substituting —CH_3 , —Cl , or $\text{CH}_2\cdot\text{COO—}$ in one of the methylene groups, and increased by the substitution of —CN or $\text{—CO}\cdot\text{O}\cdot\text{CH}_3$. The tendency of the substituting groups to add electrons to, or withdraw them from, the double bond is thus seen to be in the same direction as in the electromeric effect that governs aromatic substitution. Bernstein (7) has also discussed theoretically the effect on the vibration frequencies of complex molecules of substitution involving configurational and symmetry changes.

A knowledge of the vibrations of the infinite methylene chain is required to interpret the spectra of long molecules and linear polymers. Theoretical treatments of this problem were given by Kellner (8) and by Barrow (9). The former author found that of 18 possible vibrations only five are active in the infrared. He obtained satisfactory agreement with the observed spectrum of polythene. Barrow used a valence force potential function and identified two $\text{—CH}_2\text{—}$ rocking frequencies, a Raman frequency at 1135 cm^{-1} and an infrared frequency at 740 cm^{-1} .

Technique.—A remarkable increase in the resolution attainable with prism instruments has been achieved by Walsh (10) in his device for converting a single into a double or multiple monochromator, in which some of the once-dispersed radiation is reflected back again through the dispersing system by means of a suitably placed reflecting device. The radiation which undergoes second order or multiple reflection is chopped and is thereby easily separated from the primary beam on emerging from the exit slit. The resulting spectrum from a conventional prism instrument modified in this way shows great improvement in resolving power and freedom from background and stray light. Jaffe (11) has drawn attention to the possible use of the Fabry-Perot interferometer to increase the resolution attainable in infrared work; from the published records it seems that Walsh's solution of the problem may be more promising. The design of static multislit infrared spectrometers by Golay (12) offers the combination of freedom from stray light and high speed in the recording of infrared spectra. Owing to the importance of the reflecting microscope in the application of infrared methods to biological and microcrystalline problems, the problem of its design has been receiving attention in papers such as that of Steel (13).

Intensity measurements.—There has been a steady increase in the number of careful intensity measurements and it seems that intensity spectroscopy may yet be regarded as of comparable importance to frequency spectroscopy. In addition to the theoretical interest of the relation of vibrational transition probabilities to quantities such as bond polarizability and change of dipole moment during vibration, intensity measurements are important not only in direct analytical applications, but also in the determination and identification of structure by infrared methods. Some of the studies mentioned below suggest that intensities as well as frequencies will be used to an increasing extent in the correlation of infrared bands with structural features. This point has been emphasized by Lippert & Mecke (14). Willis (15) has discussed the effect of slit width on the shape and intensity of infrared

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absorption bands and has given correcting formulae that can be used with either gaussian or triangular slit functions. In the measurement of Raman intensities, Woodward & George (16) have made the interesting observation that a correction factor of magnitude $1/n^2$ must be introduced to take into account the effect of the refractive index n of the solvent on the amount of light that is "seen" by the spectrometer. Very careful intensity measurements have been made by Callomon, McKean & Thompson (17, 18) on nitrous oxide, carbonyl sulphide, and on acetylene. They used the method of broadening the bands with varying pressures of nitrogen and extrapolating the results to zero pressure. The foreign gas not only broadened the rotational structure but also caused a marked increase in the total absorption intensity; the form of their results is such as to show the need for increased attention to be given to the theory of pressure and foreign gas effects in spectra in general. Similar careful measurements on carbon monoxide pressurized with a variety of foreign gases were carried out by Penner & Weber (19, 20). The influence of constitution on the intensities of $-\text{CH}_3$ and $=\text{CH}_2$ vibrations in a variety of ketones and esters was studied by Francis (21), who found that carbonyl and ester groups decrease the intensity of the stretching vibrations, and increase that of the deformation vibrations, of the neighbouring CH_3 and CH_2 groups. The $\text{C}=\text{O}$ stretching frequency at 1720 cm^{-1} was found to be nearly twice as intense in esters as in ketones; the same increase was noted in the case of the $\text{C}-\text{C}$ and $\text{C}-\text{O}$ stretching frequencies in groups next to the carbonyl group. An instance of the combined use of molar extinction and frequency in the analysis and identification of carbonyl compounds is to be found in the work of Cross & Rolfe (22), while Brown, Holliday & Trotter (23) have shown that it is possible to use the intensity of the OH frequency in the infrared spectrum to give a measure of the hydroxyl content and the adsorbed or imbibed water content of dry films of various cellulose derivatives. Coulson, Hales & Herington (24) applied the measurement of the height of the absorption band near 3450 cm^{-1} to the detection of water in pyridine and to its quantitative estimation in the range 0.002 per cent to 0.2 per cent; Penner (25) used intensity values in CO for the measurement of flame temperatures, while Milatz, Kluyver & Hardebol (26) describe a most interesting attempt to measure $\text{C}^{13}:\text{C}^{12}$ isotope ratios by using the infrared absorption of carbon dioxide and employing as a detector a gas cell containing pure C^{13}O_2 .

Simple molecules and vibrational assignments.—During the year there were many studies of the Raman and infrared spectra of simple molecules where it was possible to make theoretical assignments of the vibrational frequencies. Some of these studies involved careful revisions of earlier work, and it is not appropriate to describe all of them in this review. The measurement of the Raman spectrum of fluorine by Andrychuk (27) made it possible for him to determine both the rotational and vibrational constants of the fluorine molecule, and to determine its nuclear spin. A very careful analysis of the rotational structure of the 4.5μ band of nitrous oxide by Thompson & Williams (28) gave rotational constants that are now in agreement with

microwave measurements. The previous discrepancy was shown to be largely the result of incorrect wavelength measurement, and their paper emphasizes the need for the establishment of precise wavelength standards in the infrared. For the band in question, Thompson & Williams used wavelengths in the CO fundamental band calculated by Rao (29). Jones *et al.* (30) have re-examined the infrared spectrum of fluorine monoxide and have removed the discrepancy between the infrared and electron diffraction data. Pulford & Walsh (31) made a new assignment of frequencies in nitrosyl chloride and were able to get better agreement with the thermodynamic data, but still find an unexplained discrepancy between the two sets of data. The abnormally small C—C distance (1.46 Å.) that had previously been found in methylacetylene has now been confirmed by measurements on deuteromethylacetylene in the photographic infrared by Herzberg, Vallance Jones & Leitch (32). The theoretically important problem of the boron hydrides has again received attention in the form of an infrared and Raman study of the isotopic diborane molecules $B_2^{10}H_6$ and $B_2^{10}D_6$ by Lord & Nielsen (33). Their results confirm the "bridge" structure, with its protonated double bond, and the data are best fitted by a nonplanar structure of symmetry D_{2h} , although an unsymmetrical C_{2h} form cannot be definitely excluded. Halogen derivatives of ethane have been investigated by several workers. Powling & Bernstein (34) studied rotational isomerism in several chloro and bromo-derivatives, while El-Sabban *et al.* (35) made a careful infrared and Raman study of 1,1,1-trichloroethane from which they were able to calculate thermodynamic data for the molecule and to establish the internal rotation potential energy barrier as 2840 cal./mole. Complete vibrational assignments for propane and various deuteropropanes have been given by McMurray & Thornton (36), who stated what has long been known but sometimes overlooked, namely that the skeletal and rocking frequencies cannot be described in terms of individual groups, but involve interaction over the whole molecule. Diazomethane and its deuterium analogue have been found to have C_{2v} symmetry by Crawford, Fletcher & Ramsay (37) in agreement with the electron diffraction results. Ethylene oxide, ethylene imine, and ethylene sulphide have been re-examined by Thompson & Cave (38), and ethylene imine and N-methylethylene imine were studied by Hoffmann, Evans & Glockler (39), who pointed out the expected analogy between these compounds and cyclopropane and ethylene oxide. Amongst molecules of higher symmetry, the octahedral structure O_h has been confirmed for sulphur hexafluoride in the infrared by Lagemann & Jones (40) and for molybdenum and tungsten hexafluorides in a Raman study by Tanner & Duncan (41). In the case of the two latter molecules there seems to be a discrepancy between the spectroscopic and electron diffraction data.

More complex molecules.—Amongst the rather more complex molecules, Marrison (42) investigated the characteristic infrared frequencies of a number of cycloparaffins and their derivatives; Lippincott, Lord & McDonald (43) studied cyclooctatetraene and cyclooctatetraene- d_8 , where the Raman and infrared evidence strongly favours the D_4 (crown) symmetry with al-

ternating double and single bonds. Two interesting three-dimensional "cage" structures have been investigated. The hydrocarbon nortricyclene C_7H_{10} was studied by both infrared and Raman methods by Lippincott (44), who found the spectra to be consistent with the C_{3v} symmetry of a three-dimensional structure containing one three-membered ring and three five-membered rings. The other three dimensional structure is hexamethylenetetramine for which Couture-Mathieu *et al.* (45) were able to assign fundamental frequencies on the basis of their Raman investigation of an oriented single crystal.

Empirical studies.—Amongst empirical studies of a correlative nature mention should be made of the investigations of $C=O$ frequencies in aldehydic and keto acids by Grove & Willis (46), in diacyl peroxides, peresters and perbenzoic acids by Davison (47), and in the sydnone ring by Earl *et al.* (48). Flett (49) studied the infrared spectrum between 400 and 4000 cm^{-1} of 60 carboxylic acids and has suggested five bands that can be used for diagnostic purposes. A systematic infrared study of alkaloids, particularly in the regions of $-OH$, $-NH$, and $C=O$ absorption was begun by Marion, Ramsay & Jones (50); steroids have received attention from Josien, Fuson & Cary (51) and from Bladon *et al.* (52).

Biological problems and the use of polarised radiation.—Polarised infrared radiation has been used in several important biological problems, and it seems as if increasing use of this technique is to be expected in the future. In stretched polymers, such as polythene, nylon, and polyvinyl alcohol, polarised infrared made it possible for Glatt & Ellis (53) to assign frequencies to various vibrational modes of $=CH_2$, $-NH$, and $C=O$. This study is of interest because polythene can be regarded as an approximation to the infinite methylene chain. In crystals of adipic acid and diketopiperazine, polarised radiation enabled Ambrose, Elliott & Temple (54) to study the infra-red dichroism and to obtain results which were consistent with crystal structure data. Ambrose & Elliott (55, 56, 57) used similar methods to investigate the structure of polypeptides and proteins. The dichroism of the $N-H$ stretching, $N-H$ deformation, and $C=O$ stretching frequencies in synthetic polypeptides provided evidence of two forms of the polypeptide chain, the α -form being folded (and containing seven-membered hydrogen-bonded rings), and the β -form extended. They extended this work to fibrous proteins and found evidence for both the α - and β -peptide chains in silk suture, porcupine quill, elephant hair, and swan quill. On the other hand, their results in the cases of gelatin and collagen were not consistent with the presence of either the α - or β -form of the polypeptide chain, and they suggested that in these proteins another method of folding the peptide chain must be present. These authors also investigated the probable unfolding that occurs during reversible denaturation of globular proteins.

ELECTRONIC SPECTRA

Diatomic and simple inorganic molecules.—During the year there has been relatively little activity in the field of diatomic molecular spectroscopy. It

is of interest that Dieke & Tompkins (58) have completed an analysis of the $3p^3\Sigma \rightarrow 2s^3\Sigma$ bands of the isotopic tritium-containing molecules TH and T₂; the system they examined extends between 6000 and 12000 Å, and contains more than 1150 lines in 58 bands. The dissociation energy of the nitrogen molecule is a quantity of considerable importance in thermochemistry and valency theory. Douglas & Herzberg (59) tackled the problem by a careful remeasurement under high resolution of the predissociation in the Lyman-Birge-Höpfield bands. Of the three alternative values suggested in the literature, their work has eliminated 8.565 e.v. as a possibility, but still leaves the alternatives of 9.756 and 7.373 e.v. for the dissociation energy with some leaning towards the latter figure. The nitric oxide molecule has been investigated by both Tanaka, Seya & Mori (60) and by D'Or, de Lattre & Tarte (61). The former workers found a new absorption spectrum in the vacuum ultraviolet with an upper state that proves to be identical with the upper state of the emission bands at 6000 Å investigated by Feast (62). The latter authors found at low temperatures a diffuse absorption band system between 2360 and 2320 Å that provides evidence for the existence of the dimeric molecule N₂O₂. Sulphur hexafluoride was investigated in the vacuum region by Liu, Moe & Duncan (63). Four broad diffuse weak bands (with oscillator strengths between 0.008 and 0.002) lie between 1100 Å and 800 Å. Additions to our knowledge of the emission spectra of the halogens have been made by Durie (64) who has investigated iodine fluoride and bromine fluoride, and by Venkateswarlu (65) who has discovered a new emission band system in the neighbourhood of 2770 Å in iodine subjected to an uncondensed discharge in the presence of argon.

Theory of organic spectra.—The applications of quantum mechanical theory to organic molecules belong more properly to the section of this review dealing with the theory of molecular structure and valence. Spectroscopists, however, are directly concerned with the theoretical prediction and description of the possible electronic states, ground and excited, of a given molecule, with their at least approximate relative energies, and with the probabilities of the transitions between them. No attempt will be made here to review the present status of molecular orbital and valence bond theory; attention will be confined to a few papers of direct importance to spectroscopists. Of exceptional interest is the work of Craig and Coulson and their collaborators on the significance of configuration interaction in molecular orbital theory. In simple molecular orbital theory the electrons are assigned to individual molecular orbitals and such an assignment is termed a configuration. One configuration may give rise to a number of molecular states. If account is taken of the interaction of the electrons with one another, it is found that there is resonance between different configurations, and improved though more complex wave functions can be constructed by taking linear combinations of interacting configurations and minimising the energy in the usual way. Calculations using this method were made by Coulson & Jacobs (66) for the ground and excited states of butadiene, and a survey of the method as applied to cyclobutadiene, butadiene, benzene, and naphthalene

has been made by Coulson, Craig & Jacobs (67). The important result has emerged that the inclusion of configuration interaction in the calculations has a marked effect on the predicted energy levels, particularly excited states. It appears that while molecular orbital theory without including configuration interaction can be regarded as giving a good account of molecules in their ground states, these papers throw considerable doubt on predictions of the energies of excited states by simple theory, leaving the whole question of the prediction of spectroscopic energy levels in a most unsatisfactory position. In the words of Coulson, Craig & Jacobs (67)

Without including (configuration interaction) no satisfactory account can be given even of the sequence of energy levels. There appear to be no simple rules for determining in advance which configurations will interact most strongly with one another. . . . This is a melancholy position.

One of the more encouraging features of configuration interaction is that its inclusion has markedly improved the prediction of transition probabilities and spectral intensities. Coulson & Jacobs (66) found good agreement in the case of the first allowed transition of butadiene, calculating the oscillator strength f to be 0.6 in comparison with the experimental value of 0.53. Bevan & Craig (68) by the same method have calculated the intensity of the $A_{1g} \rightarrow E_{1u}$ transition of benzene to be $f=0.81$ as compared with the experimental value of 0.69. These treatments dispense with the need for the empirical factor of 2 or 3 which Mulliken & Rieke (69) found to be necessary in calculating transition probabilities by simple molecular orbital theory, and it is now clear that this empirical factor, an unsatisfactory feature of the simple theory, arose from the neglect of configuration interaction.

Some progress has been made in exploring the field of usefulness of the simpler, more approximate, and much less general free electron model. Nikitine & El Komoss (70) have used it to calculate positions and intensities of both the first strong transitions and also some of the higher weaker transitions of polymethine dyes. The application of the model to conjugated systems with branched chains encounters certain mathematical difficulties in determining the energy levels and the nodal form of the wave functions. Kuhn (71) has tackled this problem by studying the acoustical vibrations of a stretched membrane whose shape has been made formally similar to that of the branched conjugated chain. The free electron calculation of transition intensities in polymethine chains with various combinations of *cis* and *trans* structures was also studied by Kuhn (72). Bayliss & Rivière (74) have explored the consequences of assuming a different form for the free electron potential energy. The earliest model assumed that the π electrons of the conjugated system have the uniform potential energy of the "particle in a box" [see the review by Kimball (73)]. However the real form of the potential energy along a linear conjugated chain must be a periodic or oscillating one. If one makes reasonable assumptions about the magnitude of the screening of the nuclear charges along the chain, it is possible to calculate an approximate form of the potential energy from the known geometry

of the conjugated system. It is not possible to obtain analytical solutions of the energy levels and wave functions corresponding to these assumed potential energy contours, but Bayliss & Rivière (74) investigated the problem by numerical methods using a finite difference procedure. The results obtained for butadiene and for some simple polymethines were better than those of simple free electron theory. However, they suffered from the disadvantage that the method was still one-dimensional, although the numerical calculation of energies and orbitals corresponding to any assumed distribution of potential energy can in principle be extended to two and three dimensions, but only with a considerable increase in labour.

The semiempirical approach.—In view of the difficulties associated with an exact theory of organic spectra, considerable importance attaches to semiempirical correlations such as those of Platt, where the intercomparison of the spectra of different molecular species is made, as it were, under the close supervision of general molecular theory. In a recent paper, Platt (75) analysed the conditions under which different conjugated molecules might be expected to have similar spectra. He pointed out that near ultraviolet spectra in organic compounds are associated with two types of electrons, the π electrons of conjugated systems and the nonbonded n -electrons on hetero atoms. The topology or arrangement of double bonds and hetero atoms determines the general type of the spectrum, and the number and order of the energy levels of the molecule. Molecular symmetry determines the intensities and the transition probabilities. Two molecules may be expected to have similar spectra if they have similar conjugated systems. Platt described as isoconjugate, molecules that have the same number of atoms and π orbitals in their conjugated systems; he described them as iso- π -electronic if they have the same number of π electrons and the same general geometrical arrangement. He was able to establish what he called variconjugate sequences in which a parent molecule is modified either (a) by the substitution of saturated alkyl or hetero groups on the parent, or (b) by the replacement of carbon atoms by hetero atoms or by formally conjugated groups. The study of the trend of absorption bands in such sequences helps to assign transitions in comparison with those of the parent molecule.

In another paper, Platt (76) has extended the spectroscopic moment theory of Sklar (77) and Förster (78) to the study of intensities in the weak long wavelength transitions of aromatic compounds. In the parent hydrocarbons, such as benzene or naphthalene, these transitions are forbidden except in association with certain vibrations, and on the basis of his free electron description of the excited states of aromatic compounds Platt actually showed that the oscillating classical electrical charge corresponding to these weak transitions in the parent compound is zero. A substituent group introduces an asymmetry which leads to a finite oscillating charge and a finite probability for the electronic transition. The effect of the substituent group can be expressed in terms of what is called its spectroscopic moment. The sign of the moment may be positive or negative, and the moments of groups substituted at various positions around the aromatic system may be com-

bined vectorially. Platt used the published intensity data of a number of substituted benzenes, naphthalenes, phenanthrenes, and other aromatic systems to obtain a consistent set of moments for a number of common substituents, and he showed that it is possible to use this set to account for practically all the experimental data within experimental error.

Experimental studies in organic spectra.—McClure (79) has added to our knowledge of the triplet states of 10 aromatic compounds by measuring their absorption spectra, a sufficient concentration of the metastable triplet molecules being maintained by subjecting the samples to intense transverse ultraviolet irradiation. Schüler & Reinebeck (80) continued their work on the excitation of emission spectra by electron impact. Using benzene at different partial pressures in a stream of helium, the character of the emission spectrum from the positive column of the glow discharge in helium changes. At very low benzene pressure, the emission is mainly due to molecular fragments such as C_2 , H_2 , and CH , indicating extensive destruction of the benzene by electron impact. At the highest partial pressure they employed, they found emission from excited benzene molecules in the 2600 Å region and possibly in the 3400 Å region of the triplet state; intermediate benzene pressures gave unidentified spectra that probably arise from aromatic radicals. Pyridine and related compounds continue to attract attention. Halverson & Hirt (81) completed an investigation of the diazines whose absorption spectra in the near ultraviolet consist of a sharp system near $30,000\text{ cm}^{-1}$ and a diffuse system near $40,000\text{ cm}^{-1}$. The former is regarded as an $n\text{-}\pi$ transition involving a nonbonding electron on the hetero atom, and the latter is identified as a $\pi\text{-}\pi$ transition. They used the observed frequencies to estimate the values of the C—C, C—N, and N—N exchange integrals to be used in the theoretical treatment of these systems.

There have been other investigations of interest in which systematic observations were made of the spectra within series of related compounds in order to determine the effect of substituent groups and constitutional changes in a systematic but empirical way. For example, Walba & Branch (82) examined the effect of substituents on N-substituted *p*-aminotriphenylmethyl ions. Bohlmann began systematic studies on series of phenylhydrazones and semicarbazones (83) and also on diacetylene derivatives (84), particularly polyene chains with a diacetylene grouping in the middle of the chain. It is rather surprising to find that, compared with the parent polyene, a polyene containing a diacetylene group has its ultraviolet absorption at higher frequency with a lower maximum and a rather broader absorption region. Various derivatives of *cis*- and *trans*-stilbene were examined by Calvin & Alter (85). All the *trans* compounds have a fairly intense featureless absorption band in the region 300 to 400 $m\mu$; the *cis* compounds have a much weaker band at rather higher frequency. Other systematic studies that have been made are those on fluorobenzene and substituted fluorobenzenes by Smith & Turton (86), on mono- and 2,6-disubstituted derivatives of benzoic acid by Moser & Kohlenberg (87) and the effect of a number of substituents in the series of compounds *o*-, *m*-, and *p*-X·C₆H₄·NY by

Grammaticakis (88). Brooker, White & Sprague (89) have drawn attention to anomalies in the spectra of symmetrical cyanine dyes with highly basic nuclei such as those derived from 3-methylisoquinoline; the effect of replacing a methine group by —N= in cyanine dyes was studied by Knott & Williams (90).

The far ultraviolet.—Several interesting investigations in the vacuum ultraviolet region appeared during the year. Pickett and her collaborators have begun the investigation of a series of organic compounds paying careful attention to intensities as well as to wave lengths. Pickett, Muntz & McPherson (91) investigated cyclohexane, cyclohexene, cyclopentane, cyclopentene, and benzene. Pickett, Hoeflich & Liu (92) observed the spectra of furan, tetrahydrofuran, tetrahydropyran, and dioxane. A remarkable feature of the vacuum absorption of the cyclic ethers is the pronounced vibrational structure that is observed in all cases. The low frequency of the vibration suggested that it must arise from a ring-puckering mode associated with the heterocyclic oxygen atom. Teegan & Walsh (93) found two Rydberg series in the far ultraviolet absorption of dichlorethylene. One of these was identified as being due to transitions of a π electron from the C=C double bond and gave a series converging to ionisation at 9.46 e.v. The other series was identified as belonging to the excitation of an orbital electron of one of the chlorines and converged to 10.4 e.v. The absorption spectrum of ketene was studied by Price, Teegan & Walsh (94) and was found to consist mainly of transitions to five Rydberg states in the region 830 \AA to 1370 \AA and converging to ionisation at 9.60 e.v. The spectrum was very similar to the main series of ethylene and was found to have almost identical term values.

THE EFFECT OF ENVIRONMENT

In contrast with the "idealized" spectroscopy of the isolated atom or molecule, this section deals with the effect on spectral transitions of a closely surrounding environment, as in the case of compressed gases, liquids, and crystalline solids. Some of the effects that are observed can be explained, at any rate approximately, in physical terms; others seem to require the existence of at least transitory chemical interaction with the surroundings; still others admit of no simple explanation at the present time. The literature contains a mass of unco-ordinated information with relatively few synthesising generalisations—a situation that is not surprising in view of the theoretical difficulties associated with condensed states.

Gas pressure effects.—The effect of pressure on the broadening of spectral lines was reviewed some time ago by Margenau & Watson (95); more recently Van Vleck & Margenau (96) discussed collision theories of pressure broadening, while this year Margenau (97) has published a brief treatment of the statistical theory as applied to spectral line contours. Although pressurizing with an inert gas is frequently used to blur out rotational structure in the measurement of infrared intensities, the detailed effects are not clearly understood as in the case already referred to of nitrous oxide [Callomon,

McKean & Thompson (17)]. Crawford *et al.* (98) found that infrared absorption could be induced in hydrogen when mixed with inert gases at high pressure; the effect is regarded as caused by overlap forces that come into play during close collisions. Welsh, Pashler & Dunn (99) studied the 3.3μ band of methane in the presence of helium, argon, and nitrogen at high pressure. The absorption intensity is increased by 20 per cent in nitrogen at 600 atm., and the increase in the absorption coefficient varies linearly with the density of the foreign gas. The authors could account for the order of magnitude of the effect in terms of a polarisation interaction, reminiscent of the Onsager reaction field (100), in which the oscillating dipole of the absorber induces dipoles in the foreign gas molecules; these in turn react again on the absorber to increase its effective dipole.

The solid state.—Owing to the symmetry of the crystal lattice, spectra in the solid state occupy a special place in the study of environmental effects. The subject has been referred to in these Reviews by Crawford & Mann (101). More recently Winston (102) has used group theory in connection with the spectra of rare earth salts and of benzene to discuss the two expected types of splitting of energy levels—the well-known Bethe splitting of degenerate levels, and the Davydov splitting that can occur with non-degenerate levels. It has been pointed out by Hrostowski & Pimentel (103) that the infrared spectrum of the solid phase may differ from that in the gas because of (a) the effect of the symmetry of the molecular site, and (b) the coupling of vibrations in a lattice of identical systems. It should be possible to separate these effects by studying a molecule *A* in dilute solid solution in an isomorphous substance *A*. On the experimental side, Reding & Hornig (104) have studied solid films of ammonia and deuterioammonia in the infrared, and have interpreted their results in terms of potential functions of individual molecules with weak lattice coupling, and without the need to postulate dimers or higher polymers. Hellwege & Kahle have published papers on the absorption of crystalline europium chloride 6-hydrate (105) and europium bromate 9-hydrate (106), in the latter of which they show how optical spectroscopic evidence can show a crystal to be only pseudo-hexagonal where x-ray analysis could not detect the difference from true hexagonal symmetry.

Spectra in liquid solutions.—The literature in this field contains a mass of information, largely unco-ordinated and often scattered. Reviews, not very recent, have been published by Scheibe (107) and by Sheppard (108). The most general effect of a solvent, which always seems to be present in those cases where there is no reason to suspect complexity, is to displace the absorption to lower frequencies as compared to the gas, and often to increase the intensity. Different formulae for the intensity effect have been given by Chako (109) and by Kuhn (110), and while solvents would be expected to increase the probability of transitions that are weak or forbidden, there is some doubt on experimental grounds whether there is any increase in the intensity of intense, allowed transitions [Mulliken & Rieke (69); Jacobs & Platt (110a)]. The red displacement has long been related to the

refractive index n of the solvent, or to its dielectric constant D , and is the result of electrostatic polarisation interaction [Sheppard (108)]. A simplified theoretical treatment by Bayliss (111) predicts that the red shift for electronic spectra should be proportional to the factor $(n^2-1)/(2n^2+1)$, and that its magnitude should be related to the intensity of the transition. In the infrared, Jones & Badger (112) have found that the normal solvent displacement of the third harmonic OH band of methanol is proportional to $(D-1)/(2D+1)$; but that anomalies, possibly caused by hydrogen bonding, occur in aromatic solvents. In the visible spectrum of rubrene, Badger & Pearce (113) found agreement with the factor $(n^2-1)/(2n^2+1)$, and also that the red shift at low temperature (-180°C.) could be explained by the increase in solvent refractive index. The same refractive index factor was found adequate by Coggeshall & Pozefsky (114) in a series of condensed aromatic hydrocarbons, in which they also found the magnitude of the red shift to depend on the type of transition.

On the other hand, Brooker *et al.* (115) found spectral shifts in merocyanine dyes dissolved in water-pyridine mixtures that seem inexplicable on any simple polarisation theory, and that are postulated by Brooker to depend on the effect of the solvent dielectric constant in stabilizing different polar resonance structures of the dye. The spectra of many dyes are very sensitive to concentration, probably owing to dimerization or polymerization [Sheppard (108); Michaelis (116)]. Attempts to relate solvent effects in diatomic spectra to the change in the molecular potential energy curve in the condensed state have been made by Bayliss & Rees (117) and by Warhurst (118).

Interaction spectra.—There are many examples of intense spectral absorption in the visible or near ultraviolet that arises from the presence together in solution of complex ions of certain metals in two valence states. A well-known instance is the intense brown colour of solutions containing a mixture of the chloro complexes of copper (I) and copper (II). In this case, McConnell & Davidson (119) found this absorption to be distinct from the absorption of either copper (I) or copper (II) alone, and its intensity to be proportional to the product of the concentrations of the copper (I) and copper (II) ions. They suggested that the absorption is due to the presence of an interaction dimer containing some such structure as $\text{Cl} \dots \text{Cu} \dots \text{Cl} \dots \text{Cu} \dots \text{Cl}$ and that the spectrum is of the electron transfer type. This is supported by the fact that the interaction complex is probably present at only very low concentration in the solution and that the extinction coefficient of its absorption is very high. There is, for example, no evidence for the presence of such a complex in the effect of copper (II) on the solubility of copper (I) chloride. Similar examples of interaction were found between tin (II) and tin (IV) in hydrochloric acid by Browne, Craig & Davidson (120), and between iron (II) and iron (III), also in hydrochloric acid, by McConnell & Davidson (121). The conditions under which interaction can occur are not yet quite clear, since the hexacyanato complexes of iron (II) and iron (III) were found by Ibers & Davidson (122) to show no interaction.

Halogen complex ions often seem to be necessary but Ibers & Davidson found no interaction between manganese (II) and manganese (III) under similar conditions. An attempt to determine more precisely the nature of the complex was made by Craig & Davidson (123) by measuring radiochemically the photochemical exchange between tin (II) and tin (IV). The quantum yield was only 0.2, demonstrating that the electron transfer cannot involve an excited state that is symmetrical with respect to the two tin atoms. Similar interaction has been found in solids [Cohen & Davidson (124); Yamada (125)]. Dwyer, Gyarfas & Mellor (126) found no evidence of optical interaction in the visible region in solutions containing complex perchlorates of osmium (II) and osmium (III). Weyl (127) has briefly referred to the importance of these valency state interactions in connection with the colours of iron-containing minerals and glasses, and he claims that the data indicate that interaction can occur over distances of many atomic diameters.

Absorption in halogen-aromatic and similar systems.—During the year a number of papers have appeared on the intense ultraviolet absorption that is found in solutions containing halogens together with aromatic compounds, such as benzene, following on the original work of Benesi & Hildebrand (128) in which this absorption was attributed to the formation of a 1:1 complex between iodine and the aromatic molecule. [See also Hildebrand & Scott (129); Buff & Kirkwood (130).] Work during this year has indicated that similar interaction with aromatic molecules can occur with solutes other than the halogens.

Andrews & Keefer (131) investigated the case of chlorine in both benzene and *m*-xylene and found intense absorption in the neighbourhood of 290 $m\mu$. The same authors (132) later showed that solutions of sulphur dioxide in aromatic solvents such as benzene and mesitylene show relatively intense absorption in the same region of the spectrum, and with a concentration dependence which conforms to the requirements for a 1:1 complex.

Adopting Benesi & Hildebrand's explanation of the complexes as being due to acid-base interaction, Andrews & Keefer placed the ability to function as Lewis acids in the following increasing order: Cl_2 , SO_2 , Br_2 , I_2 , ICl .

Ketelaar, van de Stolpe & Gersmann (133) attributed the greatly displaced visible absorption of iodine in dioxane to a 1:1 complex whose heat of formation is 2700 cal./mole. Interaction between naphthalene and both bromine and iodine was described by Blake, Winston & Patterson (134). They showed that the position and intensity of the interaction absorption bands in all these cases depended much more on the aromatic member of the complex than on the halogen member, and suggested that the perturbing effect of the halogen is to cause a mixing of the upper level of the lowest frequency absorption with the V level at higher energy. They used perturbation theory to calculate the oscillator strengths of the interaction absorption, and obtained good agreement with experiment in the case of the naphthalene complex and bad agreement in the case of benzene. An examination of the problem in the infrared was described by Pimentel, Jura & Grotz (135) who

found that mesitylene bands normally inactive in the gas phase were observed in mesitylene solutions that contained iodine or magnesium laurate. The interaction caused an obvious breakdown of the selection rules with the production of a symmetry lower than C_{3v} , which can be explained only if the complexing molecule is located off the three-fold symmetry axis of the mesitylene molecule.

Oxalyl chloride has been added to the list of substances which can apparently form complexes with benzene by Saksena & Kagarise (136) who found new absorption in the region 360–280 $m\mu$ in solutions of oxalyl chloride in benzene, and they showed in the usual way that the data were consistent with the formation of a 1:1 complex. However, their investigation (137) of the infrared and Raman spectra of the same solutions showed no new lines that could be attributed to complex formation, and no effects that could not be interpreted as due to physical solvent effects. Mulliken (138) published a preliminary account of the quantum theory of complexes between Lewis acids and Lewis bases. He predicted the existence of a ground state and excited state whose wave functions ψ_N and ψ_E respectively could be built up from the "no bond" function ψ_0 and the "dative bond" function ψ_1 as follows—

$$\psi_N = a\psi_0 + b\psi_1 + \dots$$

$$\psi_E = a'\psi_1 - b'\psi_0 + \dots$$

The theory leads to the prediction of an intense charge transfer transition $\psi_N \rightarrow \psi_E$.

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POLAROGRAPHY AND ELECTRODE PROCESSES¹

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It is a well-known fact that electrode processes in aqueous solutions yield thermodynamic potentials only when no current is passing.

Working electrodes exhibit highly complex specific phenomena, and the elucidation of the mechanism of any particular anodic or cathodic process constitutes a formidable physicochemical problem (1).

The Nernst equation for a reversible electrode potential cannot, therefore, be generally applied to an analysis of polarographic reductions in which measurements are always made with a small current flow. Instead the problem must be treated as a kinetic one. The fact that an analysis utilizing the Nernst equation and leading to the Heyrovsky-Ilkovic equation has been successful in many instances (2, 3) would suggest that the kinetic treatment must lead to the Heyrovsky-Ilkovic equation, as a limiting solution, and this is actually found to be true.

In the reduction of a molecule or ion, X, to a substance Y, the following processes may all play an important role, and may have to be considered in a kinetic treatment:

(a) Substance X may actually not be reducible, but conversion to another substance X' must precede reduction; (b) diffusion of X (and X', where applicable) from the bulk of the solution to the electrode surface; this is the rate-determining process for "reversible" reductions; (c) adsorption of X at the electrode surface; (d) slow electron transfer reaction, which is probably the most common cause of "irreversible" reductions; (e) desorption of Y from the electrode surface; (f) diffusion of Y away from the surface; (g) the initial product may be a substance Y', rather than Y, and the conversion of one to the other may be important; (h) adsorption and desorption of extraneous substances may interfere with the reaction being studied; (i) any reduction involving more than one electron may actually occur in steps (even though it gives a single wave); each step may then involve some of the preceding processes.

The general problem of the kinetics of electrode processes is still largely unsolved (4). For the reduction of hydrogen ion on various electrodes, for example, several slow electron transfer reactions have been considered, as well as processes of type (e) and (g), in addition to the diffusion processes, and it is still uncertain which of these are rate-determining under various conditions. For other electrode processes the present state of knowledge is even less satisfactory.

¹ The survey of the literature pertaining to this review was concluded in December, 1951.

It cannot be expected, therefore, that we should have certain knowledge of any polarographic processes. However, in the last few years, fairly detailed mathematical analysis of some special cases has been made, and the equations derived in each case are found to be applicable to some known examples.

From the theoretical studies made so far it appears that two important generalizations can be made. First, except where a slow chemical process of type (a) plays a predominant role, a limiting current should be obtained at sufficiently high potentials which corresponds to a zero surface concentration of reducible substance, and which obeys the Ilkovic equation (3), or, more strictly, one of its modifications (5, 6). In other words, the value of the limiting current as an analytical tool is unimpaired.

Second, suitable limiting conditions always lead to the well-known characteristics of the "reversible" polarographic wave. The required conditions are usually that all processes are rapid compared to diffusion. Where processes of type (g) and (i) are of importance, however, the situation is more complicated.

However, dangers in the interpretation of experimental data exist. Where a slow chemical process of type (a) exists, a limiting current is obtained, but it does not obey the Ilkovic equation. Where there is a slow electron transfer reaction, a plot of $\log i/(i_a - i)$ versus applied potential may yield a straight line (as it does for "reversible" reductions), but the slope of this line no longer carries the same significance.

Slow chemical processes.—A discussion of the effects of a slow chemical reaction of type (a), leading to a kinetic limiting current which does not obey the Ilkovic equation, was first given by Brdicka & Wiesner (7). Their

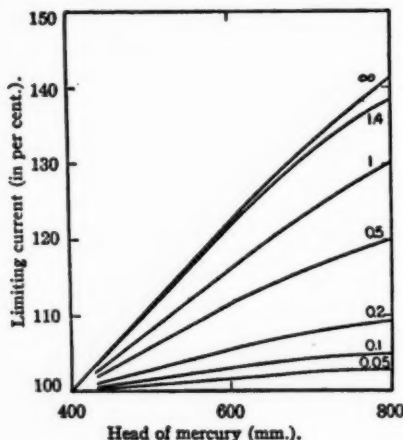


FIG. 1. Variation of instantaneous limiting current as a function of the head of mercury for different values of $kD^{-1/2}$. $kD^{-1/2}$ is expressed in $\text{sec.}^{-1/2}$. Current is in percentage of the value for $H=400$ mm. [Delahay (8)].

treatment, however, assumes that the chemical reaction occurs only at the electrode surface so that it is limited to heterogeneous reactions. The mathematical development is made only for the limiting current (surface concentration of $X' = 0$).

An extension of these ideas has been made by Delahay (8). He has shown that the limiting value of the average current increases with drop time, but that the amount of this increase depends on the rate constant, k , of the heterogeneous reaction. Where $k/D^{1/2}$ is smaller than 0.05 the limiting current is virtually independent of drop time (between 1 and 4 sec.); where $k/D^{1/2}$ is greater than five on the other hand, the limiting current approaches the value for an infinite k ; i.e., the Ilkovic equation is obeyed.

According to the treatment of Brdicka & Wiesner (7) the limiting current for reaction-controlled reduction is always independent of the height of the mercury column, but Delahay shows that this is true only where $k/D^{1/2}$ is smaller than 0.05. The relation between current and mercury head for other values of $k/D^{1/2}$ is shown in Figure 1.

Both Brdicka & Wiesner and Delahay have applied their considerations to the reduction of pyruvate ion at the potential characteristic of pyruvic acid.² Here the reaction step is



the rate of which at the surface would be proportional to the product of the surface concentrations of pyruvate and hydronium ions. The currents were found to obey the theoretical pH dependence, and rate constants were calculated from the data.

It is quite clear, however, and has been recognized by Brdicka, that the theoretical treatment given cannot actually be applied to this particular reduction, for reaction I is not heterogeneous, but, instead, occurs throughout the solution. Furthermore, except at the electrode surface, where the concentration of HA is zero (since we are concerned with limiting currents only), the reverse reaction of I also occurs.

A rigorous formulation of the problem must therefore involve the solution of simultaneous equations of the form

$$\begin{aligned} \frac{\partial(HA)}{\partial t} &= D \frac{\partial^2(HA)}{\partial x^2} + k_1(H^+)(A^-) - k_2(HA) \\ \frac{\partial(A^-)}{\partial t} &= D' \frac{\partial^2(A^-)}{\partial x^2} - k_1(H^+)(A^-) + k_2(HA). \end{aligned} \quad 1.$$

The constants k_1 and k_2 are not independent, but their ratio, k_1/k_2 , must be equal to the ionization constant of pyruvic acid.

A solution of these equations has been obtained by means of Laplace transformations by Kouřtecký & Brdicka (9). Their treatment actually goes further than suggested here, for it takes into account the fact that proton donors other than the hydronium ion may participate in the conversion of pyruvate to pyruvic acid.

² Two waves are obtained, one corresponding to the reduction of the acid, the other to the reduction of the anion.

The rate constant, in (moles/liter)⁻¹, of reaction I, assuming H₃O⁺ as the only proton donor, was found to be 1.4×10^9 . The rate constant required for the same reaction by Delahay is several hundred times greater, as is to be expected if the reaction is unrealistically restricted to the surface of the drop.

It should be mentioned here that neither the Koutecky-Brdicka treatment (9) nor any other theoretical treatment can be completely rigorous for application to the dropping mercury electrode until the simple problem of diffusion to such electrode has been solved. The treatment of MacGillavry & Rideal (10) and the suggested improvements (5, 6) are not entirely valid. It appears, however, that the errors involved affect only the value of the diffusion current constant and its dependence on capillary characteristics, which we need not be concerned with here.

The polarographic behavior of α -halogenated organic acids differs from that of pyruvic acid in that only one wave is observed instead of two. This fact and the observed variation of half-wave potential with pH can, however, be explained very simply by the same method that was used for the reduction of pyruvic acid with the additional postulates that the recombination reaction I is very fast and that the electron transfer reaction is slow. The latter requires a treatment by the method given below. Essentially this treatment has been given by Saito (11).

Such a treatment does not lead to an S-shaped relation between $E_{1/2}$ and pH, as suggested by Elving and co-workers (12) but instead to a superficially similar relation in which the main portion is a straight line, as indicated by Saito.

The simplified treatment of Brdicka & Wiesner has been extended by Hanus & Brdicka (13) to the limiting currents in the reduction of dibasic acids and their anions. The discussion is limited to the pH range in which only the two anions are present in the body of the solution. Two waves should then be observed: the first due to the reduction of H₂A formed by recombination:



the second, at a more negative potential, due to the reduction of HA⁻. Reaction II is supposed to be very rapid, so that equilibrium between A⁻ and HA⁻ exists at the electrode surface. Where i_1 and i_2 represent the limiting currents of the two waves (their sum would be the total diffusion current), Hanus & Brdicka find that

$$\frac{i_1}{i_2} = \frac{(a_{H^+})^2}{K_2'(a_{H^+} + K_2)} \quad 2.$$

where a_{H^+} is the hydrogen ion activity, K_2 is the second dissociation constant of H₂A, and K_2' is a constant involving the rate constant of reaction III, the mean diffusion constant and the capillary characteristics. This equation is verified in experiments with maleic, citraconic, and fumaric acids. In the last named the second wave occurs at too negative a potential to be observed, but

equation 2 can still be applied since $i_2 = i_d - i_1$, both of which are known.

It is of interest that equation 2 leads to an S-shaped curve for $i_1/(i_1 + i_2)$ versus pH. Where the rate of reaction III is relatively small, the shape of the curve is identical to an equilibrium curve, i.e., $i_1/(i_1 + i_2) = a_{H^+}/(K + a_{H^+})$. Where reaction III is relatively rapid, however, the curve becomes twice as steep: $i_1/(i_1 + i_2) = (a_{H^+})^2/(K + a_{H^+}^2)$. (Here K is a constant combining both K_2 and K_1' .)

Among recent interesting applications of the Koutecky-Brdicka treatment has been that of Koryta (14) who examined the role of the dissociation of Cd-nitritotriacetate complexes by hydrogen ion in the polarographic reduction of these complexes.

Slow electron transfer reactions.—The most straightforward approach to the treatment of slow electrode processes has been developed independently by a number of different authors (15 to 20). The treatment is based on the absolute reaction rate theory for electrode processes (21) and begins with the unquestionable fact that the reduction process must be reversible,



and that the net rate must be the difference between the rates of forward and backward reactions. It should be noted here that in a kinetic treatment all individual processes must be reversible, but that this does not imply over-all thermodynamic "reversibility." Only in the case of diffusion is it unnecessary to take specific notice of such reversibility, since the reversible motion of molecules under a concentration gradient is already incorporated into the laws of diffusion. It should also be noted that reaction IV is, of course, always accompanied by a corresponding process at the reference electrode.

Reaction IV must be supposed to be capable of occurring in the absence of any applied potential. Let the forward and backward rate constants in the absence of an applied potential be k_1 and k_2 . Once again these constants are not independent, but

$$k_1/k_2 = K = e^{nFE^0/RT} \quad 3.$$

where n is the number of electrons involved in reaction IV and E^0 is the standard electrode potential of the reaction in the forward direction (i.e., it is a standard reduction potential). A negative value indicates that X is less easily reduced than the substance reduced at the reference electrode.

The effect of a negative potential is to increase the net rate of reduction. To formulate this mathematically requires a knowledge of the reaction mechanism, which, as has already been stated, is not available. The simplest assumption which can be made is that reaction IV occurs as a single step, i.e., that there is only one potential barrier in the path of reduction. It is unnecessary to specify whether an applied potential increases the net rate by increasing the forward rate, or by decreasing the backward rate. Instead we assign a fraction α of the effect to the forward reaction, and a fraction $1-\alpha$ to the reverse reaction, where α may take on any value between zero and one.

The net rate of reduction, converted into units of current by the factor nFA , where A is the electrode surface area and F the Faraday, is

$$i = nFA [C_x k_1 e^{-\alpha nEF/RT} - C_y k_2 e^{(1-\alpha)nEF/RT}]. \quad 4.$$

In this equation C_x and C_y are the concentrations of X and Y at the surface in moles per square centimeter area. Strictly speaking activities should be used instead of concentrations, but this need be taken into account only if experiments in different solvents are to be compared. In the case of Y it makes no difference whether it is soluble in the solution phase or in the mercury.

The concentration of X at the surface rapidly reaches a steady state, i.e., the net rate given by equation 4 is exactly balanced by the rate of diffusion, so that

$$i = nFA k_{Dx} (C_x^0 - C_x) \quad 5.$$

where C_x^0 is the concentration of X in the bulk of the solution and k_{Dx} is evaluated by the solution of the pertinent diffusion equation, as in the derivation of the Ilkovic equation (5, 6, 10).³

Combining equations 3, 4, and 5, we obtain

$$i = nFA k_{Dx} \frac{C_x^0 - C_y e^{(E-E^0)nF/RT}}{1 + \frac{k_{Dx}}{k_1} e^{\alpha nEF/RT}}. \quad 6.$$

It is seen at once that as E reaches a high negative value both exponentials become equal to zero and we obtain $i = i_d = k_{Dx} nFA C_x^0$, i.e. a limiting current obeying the Ilkovic equation or one of its modifications.

Furthermore, if k_1 is large enough, the second term in the denominator vanishes even for small values of E . In that event we arrive at the familiar "reversible" current-voltage curves (22). Where Y is soluble (either in the solution or the mercury) and its concentration except near the surface is zero, so that, analogous to equation 5, $i = nFA k_{Dy} C_y$, we obtain

$$\ln \frac{i}{i_d - i} = \ln \frac{k_{Dy}}{k_{Dx}} + \frac{nF}{RT} (E^0 - E) \quad 7.$$

which, with the sign convention here used, leads at 25°C. to

$$\frac{d(-E)}{d \log \frac{i}{i_d - i}} = \frac{0.059}{n}. \quad 8.$$

This linear relation between E and $\log i/(i_d - i)$ has long been considered a criterion for a "reversible" reaction. Such a linear relation is also obtained for some irreversible processes, however (see equation 9).

If now k_1 is not large enough to produce a "reversible" wave, then the current at any voltage will be smaller than that predicted by equation 7 and

³ Eyring and co-workers, assuming a constant thickness for the diffusion layer, get a value of k_{Dx} proportional to the diffusion coefficient of X. This is, of course, incorrect; approximately, k_{Dx} is proportional to $D_x^{1/2}$.

we shall get a current-voltage curve which can be calculated by equation 6 and which is illustrated by Figure 2. This curve is a typical irreversible wave. As already stated, the limiting current is the same as that for a reversible wave. All of these relations could be applied equally well to anodic waves merely by reversing reaction IV and making such subsequent changes in sign as would be necessary.

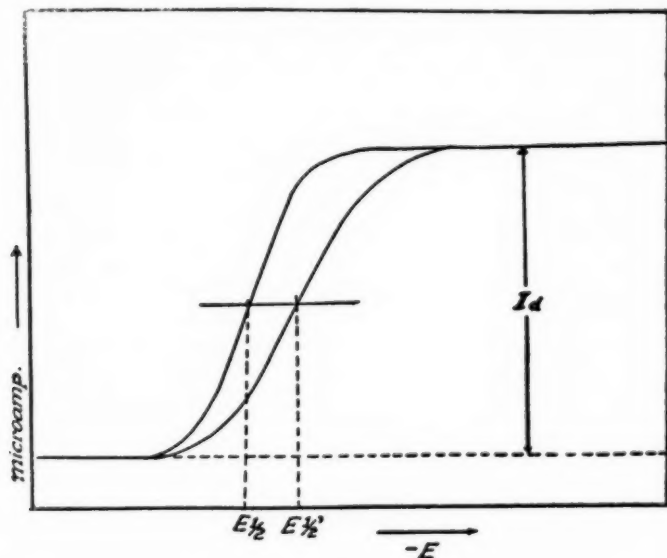


FIG. 2. Comparison of "reversible" and "irreversible" polarographic waves [Eyring, Marker & Kwok (15)].

The equations can be applied without change where E^0 is smaller or greater than zero. The remark made in this connection by Delahay & Strassner (23) is wrong and is based on a misunderstanding of the sign conventions in electrochemistry.

The most complete development of equations 4 or 6 has been made by Tanaka & Tamamushi (17). It is possible to give here only a few of their applications.

Their most important conclusion would appear to be that for processes associated with a high overvoltage, for which the second term in parentheses in equation 4 can be assumed negligible,

$$\frac{d(-E)}{d \log \frac{i}{i_d - i}} = \frac{0.059}{\alpha n} \quad 9.$$

(at 25°C.). Such an equation is known to be frequently obeyed by irreversible

polarographic processes (24). Tanaka & Tamamushi found that equation 9 is obeyed in the reduction of Ti^{+4} in acid medium and obtain $\alpha=0.6$ for this process.

Tanaka & Tamamushi have also derived equations for the case where both interaction without electron transfer (type *a*), and a slow electrode process occur. However, the reaction of type (*a*) is treated only as a surface reaction as is done by Brdicka & Wiesner, and not by the more complete method of Koutecky & Brdicka. Nevertheless, they are able to account for the pH-dependence of the half-wave potential in the reduction of pyruvic acid-pyruvate mixtures, in which they find α equal to 0.28.

They are less successful in applying a similar treatment to the reduction of metal ion complexes. They restrict themselves to the case where the successive reaction steps are decomposition of the complex ion, reduction (or oxidation) of the uncomplexed ion, and, finally, formation of a new complex ion. As before, the chemical steps are unrealistically treated as heterogeneous. This reaction scheme is clearly over-simplified, and Tanaka & Tamamushi found that it could not be applied to the reduction of nickel thiocyanate complexes, for which the polarographic waves indicate a much more complex reaction scheme.

Eyring and co-workers (15) have also treated the polarographic wave from a second standpoint, which had been found useful in the treating the overvoltage problem for hydrogen ion reduction (25). This method involves the assumption of two potential energy barriers instead of one, and leads, in place of equation 4 to the equation

$$i = nFA(C_x k_1 e^{-\alpha n \eta F/RT} - C_y k_2 e^{(1-\alpha)n \eta F/RT}) \quad 10.$$

where η , the overvoltage (with the same sign convention), has replaced the applied potential.

The attempt to use this equation, rather than equation 4, as a starting point for a theory of irreversible polarographic waves would seem to be rather speculative, especially as the validity of equation 10 is not universally accepted even for the interpretation of hydrogen overvoltage, for which it was designed (1, 4).

Using equation 10, it is again possible to obtain for a large overvoltage, an equation similar to 8,

$$\frac{d(-E)}{d \log \frac{i}{i_d - i}} = \frac{0.059}{\beta} \quad 11.$$

where β is $\alpha n/(1+\alpha)$. If this equation is assumed applicable to the reduction of titanous ion (see above), rather than equation 8, one would compute a value of 1.6 for α , which is, of course, impossible. This is strong evidence against the adoption of equation 10 rather than equation 4.

Eyring and co-workers have applied equation 10 to the reduction of nitrobenzoic acid at various pH values. However, while they observed a splitting into two waves, they failed to take into consideration the possibility

of interconversion between the acid and its anion, which almost certainly occurs here just as it does in the reduction of pyruvic acid and pyruvate. Their computations on this reaction are therefore of doubtful validity.

Delahay & Strassner (23) have also treated irreversible reductions beginning with equation 10, and have applied their conclusions to the reduction of iodate ion, calculating rate constants, free energies of activation and values of α from their data. They have apparently not realized the rather special assumptions underlying the use of equation 10. Their statement that their derivation is arrived at "without postulating any relationship between the potential of the dropping mercury electrode and the rate constant of the electrode process" and that, consequently, their analysis is "more general than previous treatments" is entirely without foundation.

Furthermore, in their discussion of the reduction of iodate ion, they failed to take into account the possibility that reactions of type (a), e.g., $\text{IO}_3^- + \text{H}^+ \rightarrow \text{HIO}_3$, may occur in the body of the solution, although this type of reaction is known to proceed with great ease, and, in fact, plays an important role in the chemistry of iodate ion (26). It is thus unlikely that there is any significance in the calculations of Delahay & Strassner, particularly in their conclusion that the rate-determining step in the reduction of the iodate involves one electron between pH 6 and pH 8, two electrons above pH 8 and between pH 6 and pH 2, and four electrons below pH 1.

An ingenious method for the estimation of α (equation 4) for reversible or nearly reversible reductions has been devised by van Cakenberghe (27). His method is based on the fact that the direct current potential at which a superimposed alternating current potential of small amplitude is unperturbed by the reactions at the mercury drop, depends on the value of α . His theoretical derivation involves the assumption that $k_{Dz} = k_{Dy}$, which is only approximately true. He finds that α is close to 0.5 for the reduction of Pb^{++} and Cd^{++} , but that it is only 0.03 for the reduction of Mn^{++} . The later reduction is irreversible, so that the result must be viewed with caution.

Adsorption.—A very convincing demonstration of the part which adsorption may play in polarographic reductions has been given by Laitinen & Onstott, from their study of the reduction of chloroplatinate (28). In the presence of camphor, which is strongly adsorbed on the mercury drop, and would prevent adsorption of chloroplatinate, the latter is reduced only at high negative potentials, in fact only beyond the desorption potential of camphor. In the absence of camphor, a polarographic wave is observed near zero applied potential (versus S.C.E.). As the potential becomes more negative, a limiting current is reached, and maintained for several tenths of a volt, but beyond -0.8 v., the current decreases sharply to a fraction of its previous value, rising again only at about -1.4 v. (Fig. 3).

Laitinen & Onstott have interpreted this phenomenon as follows. The normal reduction of chloroplatinate is highly irreversible; i.e., there is a high potential energy barrier involved. This can be circumvented by an alternative reduction process involving adsorption of chloroplatinate. The effect of potential on the adsorption of a negative ion is, however, in the opposite

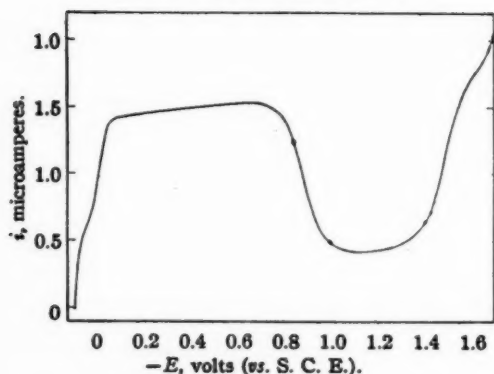


FIG. 3. Polarogram of $2 \times 10^{-4} M K_2PtCl_4$, $0.1 M KCl$ [Laitinen & Onstott (28)].

direction to the effect on its reduction. At sufficiently high negative potentials the chloroplatinate is therefore desorbed, but this high potential is still not high enough to make the rate of reduction without adsorption appreciably rapid. Thus a dip in the curve (Fig. 3) is observed.

Laitinen & Onstott analyze the problem on the basis of a reversible adsorption equilibrium. Focussing their attention on the desorption wave only, they predict that a plot of $\log (i_d - i)/i$ versus E should have a slope of $0.059/n$, i.e., a slope of 0.0296 in this case. From their experimental data, they find that this logarithmic plot is indeed a straight line, but its slope is about 0.1 instead of 0.0296. It appears then the slope is $0.059/\beta$ with β smaller than n ; i.e., we have a situation analogous to that for an irreversible reduction. A kinetic treatment of the adsorption problem would doubtless yield greater insight into its role in this particular instance, but there can be little question as to its occurrence.

Further reaction of products.—No kinetic analysis has yet been made for a reduction in which the initial reduction product undergoes further reaction, although this undoubtedly occurs in the reduction of many organic substances, such as unsaturated hydrocarbons (29) and nitro compounds (30). Several successive electron transfer steps may also be involved in these cases.

Such an analysis has, however, been made (with a number of simplifying assumptions) for the polarographic oxidation of a number of enediols, such as ascorbic acid (31, 32, 33). The oxidation waves of these compounds obey equation 6; i.e., they appear to correspond to a thermodynamically reversible reaction. Furthermore, the pH dependence of the half-wave potential (due to the fact that these compounds are acids, whose dissociation varies with pH) is exactly the same as the pH dependence of the potentiometric redox potential (E^0). On the other hand, the absolute value of E^0 determined from the half-wave potential differs by a pH-independent factor from the true value. Also, in spite of the apparent reversibility of the oxidation process,

the final product is reducible, if at all, only at much more negative potentials than expected.

These facts are all quantitatively explained if it is assumed that the reversible oxidation product is a diketone, which then reacts slowly to give a hydrated product. That the particular diketones involved (e.g., dehydroascorbic acid) are normally hydrated is in accord with their chemical properties.

A general mathematical treatment of linear systems of successive electrode reactions has been presented by Koutecky (34). Certain aspects of this treatment are at present not clear to the writers, and a full discussion must await an application to some actual processes.

Hydrogen overvoltage.—The dropping mercury electrode has been used by Kuta (35) in an effort to elucidate the mechanism for hydrogen overvoltage. He used an electrode in which the rate of mercury flow and the drop time could be varied independently. He found that the half-wave potential is independent of the former, but that it depends (in dilute HCl solutions) logarithmically on the drop time, $E_{1/2} = (RT/F) \ln t$. In more concentrated HCl solutions the relation appears to be of the form $E_{1/2} = (RT/\alpha F) \ln t$. The half-wave potential was also found for dilute solutions to be independent of concentration.

Kuta is able to explain these results by supposing either that a surface reaction between H atoms and H^+ ions is the rate-determining step in the reduction, or that the electron transfer to H^+ is slow.

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SOLUTIONS OF NONELECTROLYTES¹

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General.—Although this review will be concerned mostly with liquid solutions, the contributions of 1951 are more easily fitted into the structure of prior science, if gases are considered first. This prior science is reviewed for gases by Beattie & Stockmayer (1), and for liquids by Bell (2) and by Buff & Kirkwood (3).

The properties of a gas mixture may be expressed by the equation

$$A = \sum_i N_i [A_{i0} + RT (\ln c_i + \sum_j B_{ij} c_j + \sum_{jk} B_{ijk}' c_j c_k / 2 + \dots)] \quad 1.$$

in which A is the Helmholtz free energy, $E - TS$, R the gas constant, T the absolute temperature, N_i the number of moles of component i , and c_i its concentration, N_i/V . A_{i0} , B_{ij} , B_{ijk}' , etc. are functions of the temperature characteristic of the components designated in the subscripts; $\sum_{ij} B_{ij} c_i c_j / (\sum_k c_k)^2$ is called the second virial coefficient, $\sum_{ijk} B_{ijk}' c_i c_j c_k / (\sum_k c_k)^3$, the third virial coefficient, etc. Equation 1 is a fundamental equation in the sense of Gibbs, and all the other thermodynamic functions of the system may be obtained from it by simple mathematical operations. Equation 1 may be extended to liquids in several ways. It may be applied directly, though in this case the virial expansion is not usually the most economical and convenient expression. Equation 1 may also be applied to condensed systems well below the critical temperature with only a few terms in the summation if each A_{i0} is a function of temperature and pressure, chosen so that the B 's are all zero for the pure components at some standard temperature and pressure, and the use of the equation is limited to isothermal mixing with the volume of the mixture equal to the sum of the volumes of the components. For isothermal mixing at constant pressure it is convenient to use the corresponding expression for the Gibbs free energy $G = A + pV$

$$G = \sum_i N_i [G_{i0} + RT (\ln c_i + \sum_j B_{ij} c_j + \sum_{jk} B_{ijk}' c_j c_k / 2 + \dots)]. \quad 2.$$

If the liquids are incompressible, the B coefficients have the same values in equation 2 as in equation 1. For real systems they are generally slightly different, and to make equation 2 a fundamental equation, it is necessary to know each c_i as a function of the temperature, pressure, and composition. The corresponding free energy of mixing is given by

$$G^M = RT \sum_i N_i [\ln c_i / c_{i0} + \sum_j B_{ij} c_j + \sum_{jk} B_{ijk}' c_j c_k / 2 + \dots] \quad 3.$$

in which c_{i0} is the concentration in the pure component i , so that $c_i / c_{i0} = \phi_i$ is the volume fraction of component i . The first term $\sum_i N_i \ln \phi_i$ is the Flory-

¹ This survey of the literature pertaining to this review was concluded in January, 1952.

Huggins contribution of unequal sizes (4, 5).² To express the succeeding terms in ϕ_i we note that the assumption that A_{io} or G_{io} is a function of the pressure as well as the temperature leads to degeneracy in the B 's. This may be resolved by elimination of all but the highest set of coefficients, but more conveniently by a new set

$$G^M = \sum_i N_i \left\{ RT \ln \phi_i + \frac{1}{c_{io}} \sum_{j>i} \phi_j \left[b_{ij}^o + b_{ij}'(\phi_i - \phi_j) + \dots \right. \right. \\ \left. \left. + \sum_{k>j} \phi_k (b_{ijk}' + b_{ijk}''\phi_i + b_{ijk}'''\phi_j + b_{ijk}'''\phi_k + \dots) \right] \right\} \quad 4.$$

in which $b_{ij}^o/c_{io}c_{jo} = 2RTB_{ij}$. For nonpolar mixtures, the higher terms may be neglected to a fair approximation, and the coefficients of thermal expansion and of compressibility are so little different that the ϕ 's also are approximately independent of the temperature. Scatchard in 1937 (6) showed that $b_{ij}^o \bar{V}_i \bar{V}_j$, not b_{ij}^o , should be independent of the temperature and pressure. He noted in 1931 (7) that for nonpolar mixtures b_{ij}^o is given approximately by

$$b_{ij}^o = 2(\sqrt{E_{ci}c_{io}} - \sqrt{E_{cj}c_{jo}})^2 \quad 5.$$

in which $-E_{ci}$ is the cohesive energy per mole in the standard state, so that $-E_{ci}c_{io}$ is the cohesive energy density.

Combined with the Flory-Huggins entropy his results give (8)

$$G^M = \sum_i N_i \left(RT \ln \phi_i + \frac{1}{c_{io}} \sum_{j>i} b_{ij}^o \phi_j \right) \\ S^M = \sum_i N_i \left(-R \ln \phi_i + \frac{\alpha_o}{c_{io}} \sum_{j>i} b_{ij}^o \phi_j \right) \quad 7.$$

$$V^M = \sum_i N_i \left(\frac{\kappa_o}{c_{io}} \sum_{j>i} b_{ij}^o \phi_j \right) \quad 8.$$

in which α_o is the coefficient of thermal expansion and κ_o is the coefficient of compressibility of the unmixed components. Equation 5 and 6 have been much used by Hildebrand and his co-workers (see 9).

When the volume ratios are not very large, $\ln \phi_i/x_i$ may be expanded as a power series in x_i , the mole fraction, to give

$$G^M = \sum_i N_i \left\{ RT \ln x_i + \left[\sum_{j>i} x_j (\beta_{ij}^o + \beta_{ij}'(x_j - x_i) + \dots \right. \right. \\ \left. \left. + \sum_{k>j} x_k (\beta_{ijk}' + \beta_{ijk}''x_i + \beta_{ijk}''x_j + \beta_{ijk}''x_k + \dots) \right] \right\} \quad 9.$$

Many of the current measurements are being expressed by equation 9.

Hildebrand (10) has noted that he defined regular solutions in 1929 as those in which the entropy of mixing at constant total volume is $S^M = -R \sum_i N_i \ln x_i$, and deplores that the word has been used with many other definitions, particularly the definition of Guggenheim which corresponds to equation 9 with one β term, which is independent of the tempera-

² This is, of course, not a derivation of the Flory-Huggins equation or of any of the results which follow.

ture in the zeroth approximation but has a small positive temperature coefficient for more precise calculations (11). The situation is even more complicated than he indicates. For examples, Hildebrand & Scott (9) used Hildebrand's original definition but also, like many other workers, applied the same equation at constant total pressure; Buff & Kirkwood (3) and Rotariu, Schramke, Gilman & Hildebrand (12) defined regular solutions by equations 5 and 6; and Meares (13, 14) added equations 7 and 8 to his definition. These definitions are all attempts to describe liquid mixtures in which "orienting and chemical effects are absent" (10). The differences, which are important, arise from the assumptions about the effects of differences in the molal volumes of the components, the effects of the compressibility of liquids, and the effects of deviations from random distribution. The use of equation 5 depends upon an additional assumption of a quite different nature.

Kirkwood & Buff (15) have presented a general theory of liquid solutions starting with the relation of Gibbs' grand ensemble to fluctuations. Buff & Kirkwood (3) discussed this theory as their reference (2). They developed the theory for nonelectrolytes in the dilute solution form, which corresponds roughly to equation 3 with the B 's developed in terms of the concentration of the solute only. Their result should be particularly useful in the testing of other results to determine just what conditions are imposed on the radial distribution functions by different assumptions and approximations. It is to be hoped that methods for the more accurate calculation of radial distribution functions will be developed rapidly.

Corresponding states.—The law of corresponding states may be stated as

$$p/RTc = \Phi(T/T^*, V^*c) \quad 10.$$

for which p is the pressure, c the concentration, T^* and V^* are constants with the dimensions of temperature and volume respectively, and Φ is the same function for all substances obeying the law. Chemical engineers, who usually use T/T^* and p/p^* as independent variables, have long insisted that this expression is independent of any equation of state and better than any simple equation (16). They have also taken T^* as the critical temperature, T_c , and V^* as the critical volume, V_c , or pseudocritical volume, $RT_c/3.4 p_c$, except for hydrogen and helium, for which T^* and V^* are determined from measurements at higher temperatures (17).

Hirschfelder, Ewell & Roebuck (18) showed that the law of corresponding states follows from the relation

$$u(r) = \epsilon f(\sigma/r) \quad 11.$$

in which $u(r)$ is the mutual energy of two molecules when separated by the distance r , $-\epsilon$ is the minimum of $u(r)$, σ is the value of r corresponding to this minimum, and f is the same function for all substances which obey the law of corresponding states.

It follows from equation 2 that

$$B_{ij} = V_{ij}^* f(T/T_{ij}^*). \quad 12.$$

Guggenheim & McGlashan (19) have obtained a composite curve of B_{ii} for simpler gases from T_c to $16 T_c$, using the critical temperature and volume for all but hydrogen and helium. For B_{ij} when $j \neq i$, they made the classical assumption that $V_{ij}^* = (\sqrt[3]{V_{ii}^*} + \sqrt[3]{V_{jj}^*})^3/8$. This corresponds to $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$, which should hold exactly for hard spheres, and to a good approximation for any reasonable spherical molecules. They also made the assumption that $T_{ij}^* = (T_{ii} T_{jj})^{1/2}$. This corresponds to $\epsilon_{ij} = (\epsilon_{ii} \epsilon_{jj})^{1/2}$, which is harder to predict. Quantum mechanics (20) leads one to expect $\epsilon_{ij} \sigma_{ij}^6 = (\epsilon_{ii} \epsilon_{jj} \sigma_{ii}^6 \sigma_{jj}^6)^{1/2}$. The behavior of nearly ideal liquid solutions (7) leads to $\epsilon_{ij} / \sigma_{ij}^3 = (\epsilon_{ii} \epsilon_{jj} / \sigma_{ii}^3 \sigma_{jj}^3)^{1/2}$. The most frequently used assumptions correspond to $\epsilon_{ij} \sigma_{ij}^3 = (\epsilon_{ii} \epsilon_{jj} \sigma_{ii}^3 \sigma_{jj}^3)^{1/2}$ or $\epsilon_{ij} = (\epsilon_{ii} \epsilon_{jj})^{1/2}$. Perhaps the best justification for the last form is the success achieved by Guggenheim & McGlashan (19) in representing the second virial coefficients of mixtures. They stress the conclusions that this combination of constants depends upon the law of corresponding states, and that any equation of state using combination of constants should be consistent with this law.

In a very interesting study of mixtures Longuet-Higgins (21) has expressed equation 11 as

$$u_{ij}(r) = f_{ij} u_{oo}(g_{ij} r) \quad 13.$$

in which f_{ij} and g_{ij} are constants and $u_{oo}(g_{ij} r)$ is the mutual energy of two standard molecules at the distance $(g_{ij} r)$. He has defined conformal solutions as mixtures which conform to equation 13, and for which all parameters f_{ij} and g_{ij} are between 0.9 and 1.1 if one of the components is taken as standard. He assumed that when $i \neq j$, $g_{ij} = (g_{ii} + g_{jj})/2$, which is a good approximation for $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ when the difference is not greater than 10 per cent. He makes no assumption relating f_{ij} to f_{ii} and f_{jj} . His results require a complete knowledge of the properties of the standard component, two parameters for each other component, corresponding to T_{ii}^* and V_{ii}^* and one for each pair corresponding to T_{io}^* , or two properties of a solution may be compared from measurable properties of the standard alone. Thus

$$G^E: S^E: H^M: V^M: : E_{co}: - (\partial E_{co} / \partial T)_p: E_{so} - T(\partial E_{co} / \partial T)_p: TV_o \alpha_o \quad 14.$$

in which G^E is the excess free energy, S^E the excess entropy, H^M the change of enthalpy, and V^M the change of volume on mixing at constant temperature and pressure, E_{co} is the cohesive energy of the standard, V_o is its volume as liquid, and α_o is its coefficient of thermal expansion.

In comparing his results with experiments, Longuet-Higgins has disregarded his conditions for conformal solutions. He concluded that the entropy of solution of gases in a conformal solvent is a linear function of the enthalpy of solution, and that the line is determined by measurable properties of the solvent. He found satisfactory agreement for the solubilities of many gases in benzene, carbon tetrachloride, ethyl ether, acetone, methyl acetate, and ethanol. He found fair agreement with the measurements of Meares (13, 14) for the ratio H^M/V^M for the mixing of ethyl esters of dibasic acids in ethyl acetate and in 1:3 dibutanediol diacetate. He also checked all the relations of equation 14 for several nonpolar mixtures.

Brown & Longuet-Higgins (22) have extended the theory of conformal

solutions to the second approximation, which cannot be determined completely from properties of the standard. Barker (23) has treated dipole-dipole interactions by combining this theory with the Lennard-Jones potential and the mutual energy of two dipoles. Cook & Longuet-Higgins (24) have given a thorough comparison with the measurements by Haselden, Newitt & Shah (25) of the vapor-liquid equilibrium of ethylene-carbon dioxide mixtures. They take carbon dioxide as standard (component 1), and determine f_{22} and g_{22} from the ratios of the critical temperatures and pseudocritical volumes, and f_{12} essentially from the critical temperatures of the components and of the equimolar mixture. Equation 5 is not even approximately valid for this system. From these they determined the vapor pressure and equilibrium vapor and liquid compositions at ten-degree intervals from -30° to 10°C. , with pressures ranging from 15 to 60 atm. The agreement is satisfactory at the higher temperatures, and not so good at the lower temperatures. It is not clear whether the difficulties arise from the fact that the test system is not conformal, or from inadequacy of the theory. This reviewer would have been better satisfied with a calculation of f_{22} at each temperature from the properties of the components, and of $(2f_{12} - f_{22} - 1)$ at each temperature from the behavior of one solution. Then the source of the discrepancies would be more apparent.

An obvious extension of the Longuet-Higgins picture to molecules of different sizes is to take the analogues of equations 6, 7, and 8 with $\alpha^* b_{ij}^*$ replaced by $-db_{ij}^*/dT$, and $\kappa_0 b_{ij}^*$ replaced by $TV_0\alpha_0$. Equations 7 and 8 contain the additional approximation that $-(\partial E_c/\partial V)_T = E_c$. They were obtained only from this approximation and the assumption that $(\partial E_c/\partial T)_V = 0$, but the derivation was not simple. One very important contribution of Longuet-Higgins is his very neat, and let us hope convincing, way of expressing his results.

Nonpolar liquid mixtures.—The quasi-chemical lattice theory has been extended by Guggenheim & McGlashan, who show that the difference in entropy between spheres in a cubic or a face-centered cubic lattice and in a close packed lattice is very small (26), that the consideration of interactions of three spherical molecules at a time and of four at a time gives entropies very little different from the consideration of only pair interactions, and that the difference of any from zero excess entropy is "itself usually unimportant" (27). McGlashan (28) has studied the mixtures of spheres and double sphere molecules, and showed that successive approximations approach the Flory-Huggins value, though apparently not as an asymptote.

The great weakness of this theory is the assumption that the change in volume is zero for isothermal mixing at constant pressure, which is impossible unless the compressibility is zero. The conclusions of the theory are probably nearly correct for the entropy of isothermal mixing at constant total volume. The difference in entropy change between the two changes of state has been calculated thermodynamically by Scatchard (6) as

$$S_p - S_v = V^M \alpha_0 / \kappa_0 - \frac{V_0 d}{\kappa T d \ln T} \left[\ln \left(1 + \frac{V^M}{V_0} \right) - \frac{V^M}{V_0} \right]. \quad 15.$$

The second term is negligibly small. Therefore, the volume change on mixing is the only property of the solution which enters. Equation 15 is particularly important in comparing the results of the lattice theory with experiment, but it is seldom considered in this connection. For example, Münster, in explaining the excess entropy of mixing of benzene and cyclohexane by the orientation of benzene molecules in the pure liquid (29), discussed the change at constant pressure, which is about twice as large as the change at constant total volume. This explanation is the quantitative expression of an idea first expressed qualitatively by Scatchard, Wood & Mochel (30), but Münster also missed the fact that these authors gave up this explanation when they found that benzene-carbon tetrachloride mixtures do not show this entropy change (31). Baxendale, Enüstün & Stern (32) have made very careful measurements of the vapor pressure of benzene from solutions of diphenyl, have calculated the entropy and enthalpy changes, and have compared their results with the lattice theory, with no measurements of volume change on mixing. Van der Waals (33) has concluded the comparison of his calorimetric measurements with the vapor pressure measurements of Brønsted & Koefoed (34) with a discussion of hexane-dodecane mixtures. The importance of the volume change on mixing is brought out very clearly by the measurements of Brown & Ewald (35) of vapor pressure equilibrium in mixtures of benzene and *n*-heptane, for which they found at equal mole fractions at 70° that TS_z^E is 111 cal. at constant pressure and 15 cal. at constant total volume, while the Flory-Huggins value is 21 cal. Neglect of the volume change would give 90 cal. per mole of unexplained TS_z^E , consideration of the volume change leaves -6 cal. per mole, which is probably within the experimental error. Equation 5 gives 75 cal. for E_z^M at constant volume as compared to the measured 83 cal.

The equation of Benedict, Webb & Rubin (36) is an excellent example of the application of the same equation to both the vapor and the liquid, but with deviations from the virial form of equation 1 at high concentrations. It is

$$p = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + \alpha\alpha d^6 + \frac{cd^3}{T^2} (1 + \gamma d^2)e^{-\gamma d^2} \quad 16.$$

in which d is the molal density (or concentration), and B_0 , A_0 , C_0 , b , a , α , c , γ are empirically determined parameters. The second virial coefficient is the same as in the Beattie-Bridgman equation, and the third is nearly the same. They combined B_0 , $A_0^{1/2}$, $C_0^{1/2}$, $\gamma^{1/2}$, $b^{1/3}$, $a^{1/3}$, $c^{1/3}$, and $\alpha^{1/3}$ linearly ($B_0 = \sum x_i B_{0i}$, etc.) (37). For B_0 this corresponds to $\sigma_{ij}^3 = (\sigma_{ii}^3 + \sigma_{jj}^3)/2$, an approximation which is often used successfully. For A_0 and C_0 , their method corresponds to $\epsilon_{ij}\sigma_{ij}^3 = (\epsilon_{ii}\epsilon_{jj}\sigma_{ii}^3\sigma_{jj}^3)^{1/2}$. They have now determined parameters for 12 of the lower hydrocarbons (38), and tested the results with the measurements of vapor-liquid equilibrium for nine binary mixtures and three ternary mixtures of these hydrocarbons (39). With Friend (40) they have developed methods for using the equations to predict vapor-liquid equilibrium in any mixture of these components, with the aid of approximate rela-

tions and three hundred charts. Their results, like those of Longuet-Higgins, may be used over the whole equilibrium range to the critical temperature.

Hoge & Arnold (41) have measured the vapor pressures of mixtures of H_2 with HD and with D_2 at 17–20°K. They find positive deviations from Raoult's Law of about 3 per cent for approximately equimolal mixtures. Morrow (42) has explained the variation of the lambda temperature with composition for mixtures of He^4 and He^3 on the basis of equations 5, 6, and 7, and obtained excellent agreement which depends, however, on the choice of heat capacity.

Aroyan & Katz (43) have studied vapor-liquid equilibrium in the system hydrogen-*n*-butane. Jordan & Van Winkle (44) have studied mixtures of dodecane and octadecane from 10 mm. to 760 mm. pressure.

Barber & Cady (45) have studied the vapor-liquid equilibrium of tungsten hexafluoride-perfluoro-*n*-pentane mixtures, and Rohrback & Cady (46) that of tungsten hexafluoride-perfluorocyclopentane. For the first system the maximum excess free energy per mole is 60 cal., about half that calculated from equations 5 and 6. For the second system the measured maximum is about 50 cal. compared to 70 cal. calculated.

Rotariu, Schramke, Gilman & Hildebrand (12) have measured the solubility of mercury in phosphorus and find the solubility one-fifteenth that calculated by equations 5 and 6. The metallic nature of mercury should lead to a larger excess free energy and so to a smaller solubility. The measured solubility corresponds to an excess free energy 40 per cent greater than that calculated, which is excellent agreement for such a system.

Sieg, Crützen & Jost (47) have made a thorough study of benzene-dichloroethane, measuring the vapor-liquid equilibrium at three temperatures and at two pressures, the heat of mixing, and the heat capacities. They express their results in terms of equation 9 and find three β_{ij} terms necessary.

Reamer, Sage & Lacey have studied methane-hydrogen sulfide (48), propane-carbon dioxide (49), and methane-*n*-butane-decane (50); Reamer & Sage have studied propene-propane (51); and McKay, Reamer, Sage & Lacey have studied ethane-propane (52). Their measurements cover the temperature range 0° to 400°F. and pressures up to 10,000 lb. per sq. in.

Polar mixtures.—The adjective polar is used in two quite different meanings: first, to mean composed of molecules with permanent dipole moments; and second, to mean having hydrogens capable of forming hydrogen bonds, that is, with dipoles having one end very close to the surface. The double meaning leads to serious difficulty only when theory corresponding to the first definition and to a very short dipole, embedded in the molecule, is compared with experiments on substances described by the second. Only the second definition will be used in this review.

Haase (53) has given an empirical review in which he divides liquid mixtures into three classes: nonpolar-nonpolar, polar-nonpolar, and polar-polar. He discussed them from the point of view of equation 9, in the form

$$G_E^E = x_i x_j [\beta_{ij}^E(T) + \delta_{ij}(T, x)] \quad 17.$$

in which δ_{ij} includes all the unsymmetrical effect. He noted that for non-polar-nonpolar mixtures, δ_{ij} is small compared to β_{ij}° and $d\delta_{ij}/dT$ is not large relative to $d\beta_{ij}^\circ/dT$, but for mixtures with one or both components polar, $d\delta_{ij}/dT$ is large relative to $d\beta_{ij}^\circ/dT$ although δ_{ij} is not much larger relative to β_{ij}° than in nonpolar mixtures.

Bonnor (54) has given an improvement of Martin & Brown's (55) treatment of solutions of molecules with short central dipoles. He has taken into account the polarization of the molecule containing the dipole, though differently from Kirkwood (56). For water in methanol, ethanol, and propanol and for ethanol in *n*-heptane, he obtained more reasonable values of the molecular size than did Martin & Brown. This is a case of the first definition of polar being used in the theory and the second fitting the experiments.

Prigogine & Desmyter (57) measured vapor-liquid equilibrium in the systems: *t*-butanol-carbon tetrachloride, *t*-butanol-cyclohexane, and *t*-butanol carbon disulfide. They determined the extent of association from the measurements of infrared absorption by assuming one unbonded hydroxyl hydrogen for each molecule of monomer or polymer. They then calculated the excess free energy resulting from this association and the residual excess free energy not caused by association. They expressed this residual excess free energy by equations equivalent to equation 9 with two β terms.

Coggeshall & Saier (58) have studied the association of alcohols and phenols in carbon tetrachloride solution by measuring the infrared absorption. They treated the association as leading to linear polymers of any length, with the same constant for any reaction $A_n + A = A_{n+1}$ except when n is unity, that is, except for the formation of the dimer. This constant is almost the same for phenol and several primary alcohols, and 20 per cent greater for *t*-butanol. The constant for dimer formation is two to three times as great, except for *t*-butanol where the increase is only 40 per cent. A *t*-butyl group in the *ortho* position of a phenol has little effect on the constant for dimer formation, but prevents the formation of any higher polymers.

Davies & Hallam (59) have studied solutions of acetamide in chloroform by measuring the distribution between chloroform and water, in which acetamide forms ideal solutions, and the boiling point elevation. They interpreted their results as indicating the formation of a trimer with some dimer at higher temperatures. Since their explanation of the predominance of trimers involves a twelve-membered ring, it would be of interest to compare their results with the theory of repeated association to long chain polymers.

Dimmling & Lange (60) have measured very precisely the heats of solution and of dilution of *n*-propanol and isopropanol in water at 25° up to 0.5 *M*. They concluded that there are monomers and dimers below 0.25 *M*. and that trimers appear at higher concentrations.

Kretschmer & Wiebe (61) have measured the solubilities of propane and the butanes in ethanol from 0° to 50°C. and calculated the excess free energy and entropy and the enthalpy change on mixing.

Staveley, Johns & Moore (62) have measured the effect of several alcohols in small amounts on the solubility of water in benzene. Butanol first

gives a slight increase in the heat of solution and then a sharp decrease to about one-third that in benzene, pentanol misses the maximum but otherwise resembles butanol, but octanol causes only a gradual decrease. For all mixtures they find that the entropy of solution is a linear function of the enthalpy of solution.

Sieg, Crützen & Jost (63) have studied methanol-*n*-butyl acetate mixtures, measuring the enthalpy of mixing and the vapor-liquid equilibrium over a 40° range. They express the results as equation 9 with two constants.

Ebert, Tschamler & Kohler (64) have studied at several temperatures the systems: aniline-*n*-hexane, aniline-cyclohexane, and β,β' -dichloroethylether-methyl cyclohexane. They measured the total pressure and estimated the pressure of the first component, which is much less volatile than the second. They did not correct for deviations from perfect gas laws. Their curves for $\ln \gamma_i$ versus x_i show inflections with decrease in slope as x_i approaches zero. They stated that their measurements indicate zero slope of the asymptote, which they call Henry's law. Such behavior is most surprising from a statistical mechanical point of view. We know from the much more precise freezing point measurements that in many cases the slope remains finite to much smaller concentrations than they measured. The experimental errors should be checked very carefully before the results are accepted.

Powell & Latimer (65) have given an empirical expression for the standard entropy, \bar{S}° , of nonelectrolytes in aqueous solution

$$\bar{S}^\circ = S^{\text{int}} + \frac{1}{2}R \ln M + 10 - 0.22V_M$$

in which S^{int} is molal internal entropy (rotational, vibrational, and electronic) of the gaseous molecule, V_M is the molal volume in solution.

Welty, Gerster & Colburn (66) have studied the four component system: *n*-butane-*cis*-2-butene-furfural-water. They used the equivalent of equation 9 with two β terms, treating the water as a change in the environment of the ternary organic systems. Karr, Scheibel, Bowes & Othmer (67) have studied the ternary system acetone-chloroform-isobutylketone and treated it with equation 9 with three constants and no three component terms. Othmer, Moeller, Englund & Christopher (68) have measured the system ethanol-water and Moeller, Englund, Tsui & Othmer (69) have studied the systems ethyl ether-ethanol and ethyl ether-ethanol-water, up to 140 lb. per sq. in.

Dunning, Evans & Taylor (70) have measured the vapor pressures of aqueous sucrose solutions from 43 to 83 per cent sucrose and from 60° to 95°C.

Searles & Tamres (71) have used the heat of mixing of ethers with chloroform to measure their tendency to form hydrogen bonds. They found a linear relation between this heat and the shift in frequency of the OD band of CH₃OD in these ethers. They found that the cyclic ethers other than propylene oxide give larger effects than the acyclic ethers.

Critical mixtures.—Rowden & Rice (72) studied the system cyclohexane-aniline in the critical region and noted the enormous effects of small amounts of impurities. They find six mixtures from about 0.42 to 0.46 in mole fraction

of aniline which have the same mixing temperature within 0.003° , and for which the meniscus appears in the middle of the liquid. They measured also the differential vapor pressures of solutions in and near the critical range. They found that the fugacity of cyclohexane is greater at a mole fraction of 0.581 than at 0.545 at not more than 0.17° above the critical temperature ($29.63^\circ\text{C}.$), and greater at 0.573 than at 0.553 at not more than 0.27° above the critical. If there is any region above the critical in which the fugacity curve is horizontal, it has a very small temperature range. This is in accord with the theories of Rice.

Semenchenko & Skripov (73) found that the critical mixing of nitrobenzene-hexane and of triethylamine-water are phase transitions of the second kind, which is in accord with the theories of Semenchenko. They measured the heat capacities through the transition, more accurately for the latter system because heating can be regulated more easily than cooling. At 34.11 wt. per cent triethylamine the heat capacity is 1.12 at 17.90° and 1.56 at 19.10° , and separation into two phases begins at 19.12° .

Kohler (74) has measured the total vapor pressures of triethylamine-water systems at 0° , 10° , and $18^\circ\text{C}.$ The pressure maxima are at small mole fractions of water although the critical composition is about 0.93. The extrema of the various thermodynamic functions come at mole fractions 0.5 to 0.7. The change in enthalpy and the excess entropy are both negative, but TS^E is so much larger than H^M that G_z^E is positive. He also measured the viscosity at the same temperatures and calculated the energy of activation for viscous flow. It has a sharp maximum at mole fraction 0.8 to 0.9. The change in activation energy on mixing has the same sign as the excess free energy. This does not confirm Eyring's theory, which was doubtless set up for a much simpler system.

Metal solutions.—Elliott & Chipman have measured the electromotive force of cells with fused chloride as electrolyte and cadmium-cadmium alloy electrodes from 375° to $600^\circ\text{C}.$ (75). They studied binary alloys with lead, bismuth, antimony, and tin. They expressed the results as E and dE/dT at $500^\circ\text{C}.$, and the various thermodynamic functions which can be calculated therefrom. The different alloys show a wide variety of behavior. For cadmium-lead alloys G^E , S^E and H^M are all positive and TS^E is relatively small, for cadmium-tin all are positive, for cadmium-bismuth G^E is negative while both H^M and S^E are positive, and for cadmium-antimony all are negative. They extended these studies (76) to ternary alloys of cadmium-lead-bismuth, cadmium-lead-antimony, and cadmium-lead-tin over the same range. They calculated the activities of the components other than cadmium by the method of Darken (77).

Kleppa (78) has measured the electromotive force of similar cells with bismuth versus bismuth-gold alloys and thallium versus thallium-gold alloys and determined E and dE/dT at $700^\circ\text{C}.$ For both systems there is a large negative excess entropy. For bismuth-gold there is also a large enthalpy so the excess free energy is almost zero, for thallium-gold the enthalpy of mixing is small.

Kleppa & Weil (79) have measured the solubility of copper in liquid lead below 950°C. They calculate the differential heat of solution and the excess entropy.

Hall (80) has measured the vapor pressure of gold in gold-copper alloys from the equilibrium effusion of gold from foils in the range 1000° to 1250°C. He found $\log p$ a linear function of $1/T$ with the same slope for all alloys. He also found that the activity coefficients are independent of the composition when the mole fraction of gold is less than one-half.

McKisson & Bromley (81) have measured the heat of mixing of sodium and potassium directly for compositions corresponding to Na_2K , NaK , and NaK_2 . Ewing, Grand & Miller (82) have measured the viscosities of sodium-potassium alloys. They found that the viscosities follow the Andrade equation and that the fluidity is a linear function of the weight fraction.

Wagner (83) treated alloys from the point of view that the interaction of a metal ion with electrons is more important than the interaction with other metal ions, which are much farther away on the average. Then the effect of one solute on the activity of another is an increase if they both increase, or both decrease, the electron concentration, but a decrease of the activity if one increases the electron concentration and the other decreases it. He made quantitative calculations for the effect of thallium on the activities of potassium, lithium, and sodium and obtained very good agreement.

Total vapor pressure.—There are three schools of thought among students of vapor-liquid equilibrium. The first likes to know the temperature, pressure, liquid composition, and vapor composition; the second considers the pressure measurement relatively inaccurate and requires knowledge only of the other three; and the third considers that the vapor composition is difficult to measure and works with the temperature, pressure, and liquid composition. The first school has pretty well agreed to express the measurements as the excess free energy, and the second school has settled on the relative volatility, $\alpha = y_1x_2/x_1y_2$. The third school has a much more difficult problem, which is not yet settled to everyone's satisfaction, although it has received considerable attention for many years. If the asymptotic slopes of the total pressure versus mole fraction are known with sufficient accuracy, two b 's in equation 5 or two β 's in equation 9 can be calculated. Schulze (84) has plotted $x_1x_2/(\log p - x_1 \log p_1^\circ - x_2 \log p_2^\circ)$ versus x and claims that straight lines are obtained up to $x=0.2$, from which $\log p = (ax^2 + bx + c)/(dx + e)$ so the limiting slope may be accurately determined.

Huber (85) and Kohler (74) have claimed that the vapor-liquid relations cannot be expressed accurately enough by analytical equations which fit over the whole range. They have discussed the difficulties of integration. It is certain that the vapor-pressure equilibrium cannot be expressed exactly by a simple analytical equation. In many cases, however, a simple equation is as good as the experimental measurements. In most cases a simple equation is better than integration of the Gibbs-Duhem equation with the assumption that the vapors are perfect gases.

The problem is intensified for ternary systems. Litvinov & Kondrashova

(86) have extended the method they used for binary systems, treating a ternary as a pseudobinary. They tested the method for the system methyl iodide-acetone-carbon disulfide and noted that only 120 measurements of total pressure, 69 of them on ternaries, are sufficient to cover the field. Buchholz-Meisenheimer & Kortüm (87) have compared a number of methods with measurements on the system methylethylketone-*n*-heptane-toluene. They tried the method of Redlich & Kister (88) for calculating the equilibrium in ternary and more complex mixtures from the binary equilibria. This method is to use equation 9 without any of the terms with three or more subscripts. Scatchard (8) has discussed the similar use of equation 6, which should be better for nonpolar mixtures. Scatchard, Ticknor, Goates & McCartney (89) found that for the system methanol (component 1)—carbon tetrachloride (component 2)—benzene (component 3), equation 9 without ternary terms works satisfactorily if the mole fraction differences are expressed as $(2x_1 - 1)$ instead of $(x_1 - x_2)$ or $(x_1 - x_3)$. For binary systems, the two methods are identical. The advantage of $(2x_1 - 1)$ arises from the fact that the major effect comes from the association of methanol.

When one constant is sufficient to express the measurements on binary systems, its calculation from the total vapor pressure is simple, and the poly-component systems should be completely determined from the binary constants. Few measurements on binary systems warrant more than three constants, which can be determined from the total vapor pressure without too much difficulty. The applicability of Redlich & Kister's rule can be tested by the measurement of the total pressure of a single ternary system with about equal concentrations of each component. If the rule is insufficient, this one determination gives one ternary constant. Consideration of the deviations from the perfect gas laws up to the second virial coefficient does not add enormously to the tedium.

Miscellaneous.—Eduljee, Newitt & Weale (90) and Newitt & Weale (91) have measured the pressure-volume temperature relations of several liquid mixtures up to 5000 atm. from 0° to 60°C. They express their results by means of the Tait equation. Schulze (92) has measured the volume change on mixing for several systems.

The 1950 record for liquid phases in equilibrium was eight (93). Hildebrand (94) showed how this may be extended to nine by replacing the water by two incompatible solutions of high polymers such as methyl cellulose and polyvinyl alcohol, and presumably to any desired number by repeated splitting of the aqueous phase, and probably some of the others, with incompatible high polymers.

Blake, Winston & Patterson (95) have measured the spectra in carbon tetrachloride of mixtures of naphthalene with iodine and with bromine, and have calculated constants for the complex formation. They found that the new spectra arise from displacement of the aromatic spectra in accordance with the theory of Mulliken (96).

This review has been extremely personal because the author believes that only very personal reviews are helpful. The whole field of solid solutions has

been ignored because it so depends upon crystal structure that a proper review would require more space and more knowledge than are available to this reviewer. Otherwise the criteria for inclusion have been new ideas which seem not too unreasonable, the testing of old ideas, or experimental work of such novelty, precision, or over such a range of conditions that it may be useful in testing new ideas. It is hoped that only a few important papers have been omitted because these criteria have been applied unwisely or because the papers have not come to the reviewer's attention.

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SOLUTIONS OF ELECTROLYTES¹

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Electrolytic solutions are being studied with increasing vigor and success. During the last five years, problems have been solved which had resisted repeated attacks for several decades. The year 1951 witnessed its full share of progress. Recent successes have been due, in part, to a great need for information concerning equilibria and to the availability of new instruments. The most important factors, however, seem to be the development of new experimental techniques and procedures and a clearer understanding of the meanings of basic concepts. We are beginning, at least, to understand the meaning of solvation, and we are learning more about the differences between free ions and those bound in undissociated molecules or ion pairs.

The measurement and significance of equilibrium concentrations are especially emphasized in this review. Since several properties were used in investigations of equilibria, it was necessary to discuss those properties in diverse sections of this report. Hence it was impossible to adhere strictly to a topical outline. Discussions of conductance and activity coefficients, for example, are to be found not only under those headings but in other places as well.

ELECTROSTATIC AND STATISTICAL THEORIES

Because the electrostatic field in the immediate neighborhood of an ion may be very large, the variation of the differential dielectric constant, ϵ , with field intensity is important in electrostatic theories of solutions. The effects of these variations upon estimates of the free energy of hydration of small charged spheres has been examined by Grahame (79). In the absence of adequate knowledge of the relation between ϵ and field strength, Grahame used a family of functions selected to conform with current opinions and the limited information now available. The functions, which contain four parameters, portray ϵ of water as decreasing with the square of the field intensity for relatively weak fields and approaching a lower limit as the fields become more and more intense. Two of the parameters were evaluated empirically, one from the known value of ϵ for near-zero fields and the other from the work of Malsch (145) who experimented with very intense fields. His highest field (2.5×10^9 v. cm.⁻¹) is to be regarded as weak in comparison with that which may exist in the immediate neighborhood of an ion. For various values of the other two parameters, Grahame extrapolated existing knowledge of ϵ to very large values of the field intensity. He then integrated the functions

¹ The survey of the literature pertaining to this review was concluded in January, 1952.

to calculate the possible effects of variation of ϵ upon the theoretical calculation of the free energies of hydration of spheres of atomic dimensions [cf. Born (22)]. The effects on free energy are small. Grahame's primary objective was the study of the effects of the variation of ϵ on theoretical calculations of properties of the diffuse double layer. These effects too were small, though perhaps not small enough to be neglected under all circumstances.

Booth (21) attacked a different aspect of the problem. Using a "rough model" for the structure of liquid water, he formulated a radial distribution function, which he used to extend the method of Kirkwood (124) to the derivation of a purely theoretical equation for the integral dielectric constant as a function of field intensity. The calculation employs both the refractive index and the dipole moment of the solvent. For relatively weak fields the theory indicates that the rate of decrease of ϵ is approximately that observed by Malsch. It also nicely confirms the conclusions reached by Grahame. If the parameter b_m of Grahame's equations is adjusted to produce agreement with Booth's equation at one point (5.0×10^6 v. cm.⁻¹) instead of with Malsch's observations, and if the other parameters preferred by Grahame are retained, Grahame's method leads to a curve which is nearly identical with Booth's theoretical curve.

A new theory of molecular association in liquids has been developed by Lennard-Jones & Pople (132). Their ideas have been applied by Pople (192) to the examination of the structure of liquid water. The new theory differs from the older one of Bernal & Fowler (15) chiefly in that it depends less upon the breaking of secondary hydrogen-oxygen bonds and more upon the bending of bonds. Changes in length are also considered. At any given instant nearly all of the molecules possess their full complement of bonds—four for each water molecule. In mechanical equilibrium the bond angles are approximately the angles of a regular tetrahedron. Bending is treated quantitatively by means of force constants and other structural details determined in the earlier spectroscopic studies of isolated (gaseous) water molecules. The Bernal-Fowler concept of rigid lattices is discarded explicitly. At the time of its publication the Bernal-Fowler theory seemed to be in agreement with the radial distribution function of liquid water. Shortly thereafter new x-ray investigations were announced by Katzoff (122) and by Morgan & Warren (167). The second-shell peak was found to be smaller than had been predicted by the theory. The theory of Lennard-Jones & Pople leads to satisfactory agreement both at low and at high temperatures. Combined with Kirkwood's (124) treatment of the dielectric constant of polar liquids, it has enabled Pople to calculate values for the temperature coefficient of the dielectric constant of water which are in good agreement with experiment [cf. Oster & Kirkwood (182)]. Pople has also explained (qualitatively) volume changes accompanying fusion and the temperature variation of density.

Mayer (149), extending the virial development (for osmotic pressure) initiated by McMillan & Mayer (159), has obtained an equation for the logarithm of the activity coefficient of an ion, which is a sum of coefficients

multiplied respectively by functions of the concentrations of each of the ionic species in a solution. In general, a different radius for each ionic species would be employed. For extremely dilute solutions the equation reduces to the Debye-Hückel limiting law. For higher concentrations, however, it indicates that the activity coefficient of the i th ion depends much more upon the charges and radii of ions carrying charges of sign opposite to that of the i th ion than it does on the properties of ions bearing charges of the same sign. In preliminary comparisons (unpublished) with experimental data, the new theoretical equation has been satisfactory. Calculations are slow and laborious but tables of mathematical functions, some to be published soon, will alleviate this difficulty.

Kirkwood & Buff (125) have contributed the first installment of a new statistical-mechanical theory of solutions "applicable to all types of molecular interaction." In the treatment of solutions of electrolytes, it is employed with the radial distribution function of the Debye-Hückel theory, but avoids the troublesome charging process. In the absence of long-range forces, i.e., of coulombic forces between ions, the theory yields an expression for the osmotic pressure which is a power series in the concentration of the solute.

To explain the large compressibilities of solutions of metals, e.g., calcium, in liquid ammonia, Maybury & Coulter (148) have proposed an "expanded-metal" theory. The electrons, they suggested, are in a "conductance band" as they are in metals. Serving as "resonating covalent bonds," the electrons overcome the mutual repulsions of the solvated calcium ions. The delicately balanced forces hold the ions in a pseudo-lattice which is easily distorted. Hence, compressibility is high and viscosities are low.

EQUILIBRIA IN SOLUTIONS

METHODS OF MEASUREMENT

Many properties of solutions may, in principle, be used for the determination of degrees of dissociation, or, conversely, of the extent of complex formation. If a property is to be used successfully for the study of a reaction, it is necessary that the reaction cause a variation in that property which is (sufficiently) large in comparison with the uncertainty with which that property can be estimated in the absence of the reaction. It was possible early in the twentieth century for Arrhenius and his contemporaries to base good estimates of degrees of dissociation of weak electrolytes upon conductance measurements and various thermodynamic data. Some of the estimates made then are in satisfactory agreement with the best modern determinations. Acetic acid is a familiar example. Attempts to estimate dissociation constants of the somewhat stronger electrolytes, however, were not successful. As late as 1910 Noyes & Stewart (177), using conductance measurements, proposed a value (0.02 to 0.03) of the dissociation constant of the HSO_4^- ion which was much too large. Later Sherrill & Noyes (218), using

the same data, revised the estimate. Their value (0.012) was within 15 per cent of the best modern determinations [Harned & Owen (95)]. The improvement was due largely to their replacement of Λ_0 by Λ_e , the equivalent conductance of the free ions, thus:

$$\alpha = \Lambda/\Lambda_e. \quad 1.$$

They determined Λ_e and the required activity coefficients with the aid of the newly published papers of Debye & Hückel (48). The advances in theory which led to better understanding of sulfuric acid enabled MacInnes & Shedlovsky (143) to improve the interpretation of measurements of the conductance of solutions of acetic acid. Using methods similar to those of Sherrill & Noyes, they calculated a series of values of dissociation "constants," K , which were actually constant over a small but finite range of concentration. An interesting refinement of their procedure has now been introduced by Katchalsky, Eisenberg & Lifson (119). They improved the estimation of the activity of the undissociated acid by correcting for dimerization. Their estimates of K are nearly constant for the full concentration range covered by the data of MacInnes and Shedlovsky.

Inadequate knowledge of Λ_e may result in very large errors in K . Data of Henne & Fox (103) for trifluoroacetic acid may be used to illustrate this fact. The equivalent conductance of the acid in $9 \times 10^{-4} M$ solution is 385 ohm⁻¹ cm.² eq.⁻¹. The value of Λ_0 , found by a simple extrapolation, is 390 which is nearly the same as Λ_0 of acetic acid. The ratio, Λ/Λ_0 , which is 0.987, corresponds to a value of K' (incorrectly calculated) of 0.07. If $\Lambda_0 - \Lambda_e$ for trifluoroacetic acid is the same as for acetic acid (4.3), $\Lambda_e = 385.7$ and equation 1 leads to a K' of 0.5. If Λ_e is 0.2 per cent smaller or if Λ is 0.2 per cent larger, K' is infinite. These calculations illustrate two general principles: (a) The ratio Λ/Λ_0 can not be used for a determination of the dissociation constant of an electrolyte so strong as trifluoroacetic acid. Not even qualitative statements can be based upon "constants" determined in this way. (b) The ratio Λ/Λ_e is useful only when Λ_e can be estimated with an uncertainty definitely smaller than the difference between Λ and Λ_e . In this example a change in Λ_e of less than 0.2 per cent increased the apparent value of K' from 0.5 to ∞ .

The meanings of several terms and symbols needed for further discussion of equilibria in solution are illustrated by the following equations for the dissociation of the hypothetical electrolyte, MX,



When equilibrium exists,

$$\frac{(M^+)f_+(X^-)f_-}{(MX)f_a} = \frac{(M^+)(X^-)}{(MX)} \cdot \frac{f_+f_-}{f_a} = K. \quad 3.$$

The parentheses indicate concentrations expressed in any consistent system, e.g., mole per liter of solution, mole per kilogram of solvent, mole fraction,

etc. The f 's denote the corresponding activity coefficients; K , the thermodynamic dissociation constant; and α , the degree of dissociation. When activity coefficients are not known, it may be possible to determine the equilibrium quotient

$$\frac{(M^+)(X^-)}{(MX)} = K'. \quad 4.$$

This dissociation quotient (sometimes called the "apparent constant") varies with the stoichiometric concentration of MX. By appropriate extrapolations, the limit K of the quotient K' for zero solute concentration may sometimes be determined. The equilibrium may be described also in terms of the association quotient represented by the symbol

$$\beta = \frac{1}{K'}. \quad 5.$$

The stoichiometric activity coefficient γ_+ of ion M^+ is $(M^+)f_+/m$, where m is the stoichiometric molality of MX and (M^+) the molality of the ion itself. Hence,

$$\gamma_+ = f_+\alpha. \quad 6.$$

Similarly, the mean stoichiometric activity coefficient of the ions of the electrolyte MX is

$$\gamma_{\pm} = \alpha f_{\pm}. \quad 7.$$

It is γ_{\pm} which was defined by Lewis & Randall (134); it is f_{\pm} which is obtained from statistical theories of interionic attraction. Equation 7 is often used for the evaluation of α and of K ; indeed, all thermodynamic methods for the determination of α depend in principle, at least, upon that equation.

Equation 7 can be used for the evaluation of an equilibrium constant only when an adequate theory exists for the estimation of f_{\pm} . Its inherent limitations are similar to those of Equation 1 which requires knowledge of Λ_e . It is important to observe that lack of information concerning variations in Λ_e or in f_{\pm} caused errors of only a few per cent in early estimates of constants for the dissociation of acetic acid, that it more than doubled estimates of K for the dissociation of HSO_4^- , and that it can change even orders of magnitude of estimates for very strong electrolytes such as hydrochloric, nitric, and trifluoroacetic acids. This sensitivity of the methods, when α is nearly unity, to small errors in Λ_e , f_{\pm} and γ_{\pm} caused Redlich (198) to reject the use of conductance or any of the colligative properties for determination of equilibrium constants larger than *ca.* 0.2. For electrolytes of higher charge types the upper limits of significant values of K are even lower. As Redlich pointed out, "even a dissociation constant as low as $K=0.0045$ ascribed to zinc sulfate is highly questionable." The question concerns not merely the order of magnitude of K , but whether K can be distinguished even from in-

finity. That basic problem of an upper limit for useful values of K is still a troublesome one. As we shall see below, however, the upper limits are being raised above the values of K which Redlich doubted a few years ago.

Significant values of large dissociation constants can be obtained by the use of methods which depend upon direct measurement of the concentration of a molecular species present in small amount. Optical densities may be used if that species absorbs radiation. Similarly, measurements of intensities of Raman lines can supply important information concerning degrees of dissociation.²

It has been shown, furthermore, that equilibrium concentrations of ions present even in relatively high concentration can be determined directly from the intensities of Raman lines emitted by those ions. This characteristic of the Raman method is the result of the close proportionality of the intensity of a strong Raman line to the concentration of the molecular species which gives rise to it [cf. Redlich (198); Young & Blatz (248); Young, Maranville, and Smith (247)].

STRONG ELECTROLYTES OF UNSYMMETRICAL CHARGE TYPES

Jenkins & Monk (115) have made precise conductance measurements from which they have attempted to calculate equilibrium constants for the dissociation of ions of the type MX^{++} to ions of types M^{3+} and X^{-} , and of the type MY^{+} to ions of the types M^{3+} and Y^{-} . When the degree of dissociation, α , is large, salts of these types are especially difficult to study. There are three reasons: (a) Λ_e of two electrolytes of different charge types must be estimated for each solution, (b) the effect of each electrolyte on Λ_e of the other must be correctly estimated, and (c) Λ_0 of the intermediate ion, MY^{+} or MX^{++} , must be determined with the aid of assumptions of uncertain validity; e.g., that MY^{+} and M^{3+} are similar in size, shape, and solvation. Harned & Hudson (94) found that these assumptions are inadequate to explain the mobilities, calculated from their diffusion studies, of the ion pairs in $ZnSO_4$ and $MgSO_4$ solutions.

The dissociation constants of the intermediate ions of the six complex cobalt chlorides (.02 to .032) and sulfates (3×10^{-4} to 2×10^{-3}) investigated are so small that it was possible to restrict all of the work to solutions less than 0.0015 M and thus reduce the effects of the various uncertainties. Nevertheless, Jenkins & Monk point out that they may have done no more than to indicate the orders of magnitude of the dissociation constants. It is interesting to note that both Λ_0 and K decrease as the size of the cation increases.

Using optical absorption, Näsänen (169) has determined large dissociation constants for $CuCl^{+}$ and $CuBr^{+}$.

² The usefulness of the Raman spectrum as a tool for the measurement of concentration is in addition to its service (as a vibration spectrum) in furnishing a criterion for the existence "of the molecule as a mechanical unit" [cf. Redlich (198), p. 343].

STRONG ELECTROLYTES OF SYMMETRICAL CHARGE TYPES

After discussing uncertainties and difficulties involved in determinations of the dissociation constants of electrolytes of the 1-1 charge type, Harned & Owen (95, p. 147) added:

This difficulty is magnified in the case of a salt such as zinc sulfate, because no 2-2 electrolyte has been found to have a conductance curve which approaches the limiting law from above. We are therefore at a loss to decide just what constitutes the normal behavior of the completely dissociated 2-2 electrolyte.

Though the failure to find electrolytes whose conductivity curves approach the Onsager limiting law (180) from above has rendered difficult the making of an adequate test of the law, it has not made a test impossible. The equivalent conductances of salts whose ions are associated should approach the limiting law but should approach it from below. It has long been known, however, that the $\Lambda\sqrt{C}$ curves representing the data for the most dilute solutions of CdSO_4 , ZnSO_4 , CuSO_4 , and MgSO_4 studied by Kohlrausch, and later investigators, exhibit no tendency to obey the limiting law. In the concentration range, $C = 5 \times 10^{-4}$ to 10^{-4} *M*, Λ is nearly a linear function of \sqrt{C} but varies about twice as rapidly as the theory predicts. It follows that the $\Lambda\sqrt{C}$ curves must bend sharply in the concentration range between 0 and 10^{-4} *M* if the theory is correct. An experimental demonstration of such bending would be powerful evidence for the Onsager limiting law, but aqueous solutions more dilute than 10^{-4} *M* are not amenable to satisfactory determinations of Λ by conventional experimental methods.

Figure 1 exhibits a calculated curve showing Λ as a function of \sqrt{C} for a salt of the 2-2 charge type whose dissociation constant is 0.004₃. The curve shows the rapid change in slope which is to be expected if the equivalent conductance of the free ions conforms to the limiting law. It was calculated with the aid of activity coefficients evaluated by the approximate method used by Davies (40) and Wyatt (244). Λ_e was calculated from Wyatt's conductance equation, but for these highly dilute solutions the limiting law and the various modifications of it are almost indistinguishable. The dashed line shows the extrapolation that results from exclusive use of data for solutions more concentrated than 10^{-4} *M*. Λ_0 determined from that extrapolation is significantly larger than the value calculated (by Kohlrausch's law of independent ionic mobilities) from the equivalent conductances of the ions. Estimates resulting from such false extrapolations have been unexplained anomalies for years.

Shown in Figure 1 also are a few data for CdSO_4 contributed by Deubner & Heise (49) who employed heroic methods to measure Λ of CdSO_4 in extremely dilute solutions. They worked with a cell connected to a vacuum system which enabled them to pump gases, especially carbon dioxide, from their solvent and to distil the solvent just before it was used. Using water having a specific conductance of only 0.1×10^{-6} ohm⁻¹ cm.⁻¹, they succeeded in measuring Λ of CdSO_4 in a 2×10^{-6} *M* solution. It is obvious that Λ of

CdSO_4 does approach the limiting law and approaches it as theory predicts. Data for MgSO_4 , though not covering such a wide concentration range, are very similar to those for CdSO_4 but seem to correspond to a slightly larger dissociation constant at 18°C . It is apparent that the Onsager limiting law is obeyed by both of these salts and that the curves are in satisfactory agreement with the dissociation constants, 0.004, determined by Davies (40) for CdSO_4 at 18°C . and 0.006, determined by Dunsmore & James (56) for MgSO_4 at 25°C .

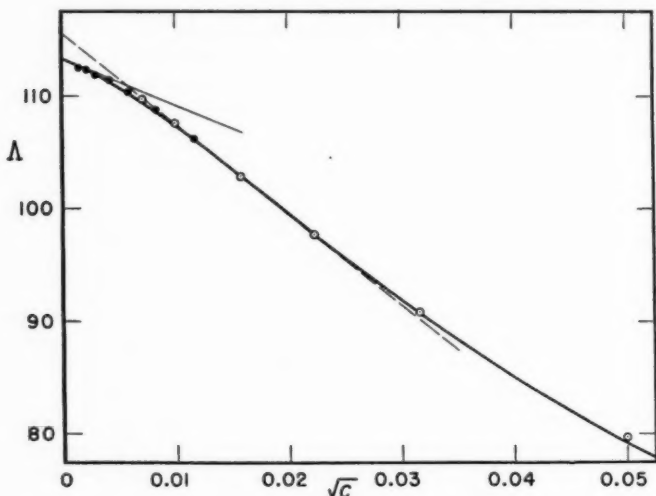


FIG. 1. Equivalent conductance ($\text{ohm}^{-1} \text{ cm.}^2 \text{ equiv.}^{-1}$) of CdSO_4 at 18°C . versus \sqrt{C} (mole^{1/2} l.^{-1/2}).

○ Kohlrausch

● Deubner & Heise

The solid straight line shows the Onsager limiting law. The dashed line shows the false extrapolation. The curve was calculated from $K=0.004$.

Strong though this evidence is, it would be tantalizingly inadequate without Näsänen's recent determination of the dissociation constant of CuSO_4 (168). Working with a region of the spectrum (ultraviolet) in which Cu^{++} does not absorb radiation, he obtained the value 0.008 (at 25°C .) from optical densities. Aware of the serious uncertainties in the assumptions underlying determinations of K from conductance data, he was gratified by the good agreement with Davies' value (0.005) calculated from Kohlrausch's data for 18°C . Davies' value corresponds to a degree of dissociation, α , of about 91 per cent and Näsänen's, to about 94 per cent in a 0.001 M solution.

In Figure 2, two series of calculations of α are compared, one from Näsänen's value of K and the other from a recent estimate (0.004_s) made by Wyatt who used conductance data of Owen & Gurry (183). Näsänen's observations leave little room for doubt that CuSO_4 is incompletely dissociated. Supplemented by the work of Deubner & Heise, they render much more plausible the calculations made by Davies and others for salts of the 2-2 charge type.

The difference between the curves is small but it is significant. According to the spectroscopic analysis, the concentration of undissociated CuSO_4 in

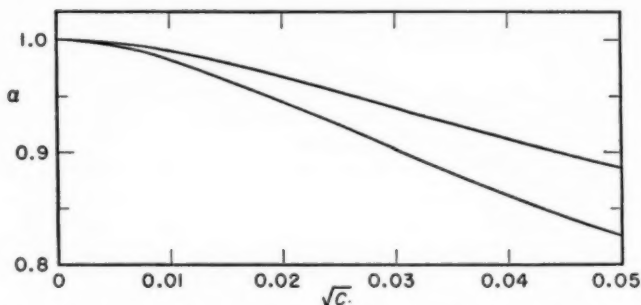


FIG. 2. The degree of dissociation, α , of CuSO_4 at 25°C. versus \sqrt{C} (mole^{1/2} l.^{-1/2}). The upper line was calculated from Näsänen's value of K (0.008_s); the lower line from Wyatt's value (0.004_s).

a 0.001 M solution is $6 \times 10^{-5} M$; according to the conductance method, it is larger, $10 \times 10^{-5} M$. If the difference is due to an error in the spectrophotometric work, it is a rather large one because the optical method provides a direct measure of the concentration of the undissociated species. If, on the other hand, the fault is in the conductance method, it corresponds to an error in Λ_s for the same solution of only 4 per cent.

An error in Λ_s of 4 per cent would lead to the calculation, from the equivalent conductance of a completely dissociated salt in a 0.001 M solution, of a K of ca. 0.02. Even with the aid of the advances made by Näsänen and by Deubner & Heise, we are still unable to distinguish with certainty between $K=0.02$ and $K=\infty$ for an electrolyte of the 2-2 charge type. Important progress has been made but basic problems remain.

There are several other interesting facts bearing upon equilibria in solutions of strong electrolytes of the 2-2 type: Purser & Stokes (196), investigating an earlier report of negative transference numbers of Zn^{++} in ZnSO_4 solutions, made new determinations by an e.m.f. method. They observed very rapid variations in the transference numbers as concentration increased from 0.1 M to 0.3 M but no negative transference numbers. Harned & Hudson (94) reported diffusion coefficients for ZnSO_4 and MgSO_4 which are much

larger than those computed theoretically for completely dissociated salts.

The anomalous absorption of supersonic energy by sea water was traced by Leonard, Combs & Skidmore (133) to the presence of MgSO_4 . [Cf. Liebermann (137).] Wilson & Leonard (243) have found the absorption to vary as the square of the concentration of MgSO_4 in a 0.003 *M* solution, but with a lower power of the concentration when $C=0.02$ *M*. This behavior suggests that the effect is dependent upon the concentration of undissociated MgSO_4 , but such a dependence has not been demonstrated.

James (112) studied the dissociation of ZnSO_4 , CuSO_4 , and zinc malonate in the mixed solvents: water-dioxane, water-acetone, water-ethylene glycol, and water-ethanol, and of $\text{LaFe}(\text{CN})_6$ in water-dioxane. A similar study was made by Dunsmore & James (56) of MgSO_4 in water-dioxane, and water-glycine mixtures and of $\text{LaFe}(\text{CN})_6$ in water-glycine. The authors found that the variation of the dissociation constants of ZnSO_4 , CuSO_4 , MgSO_4 , and $\text{LaFe}(\text{CN})_6$ with changing dielectric constant could be explained by the action of coulombic forces alone, but that the forces in zinc malonate are more complicated. James suggested that ion pairs are formed by the union of hydrated ions in solutions of the first four salts, but that "no solvent molecules can intervene between" firmly bound ions of zinc malonate. From the temperature variation of the dissociation constants of zinc malonate, James obtained -3060 cal. mole $^{-1}$ for ΔH° . ΔF° and ΔH° are therefore of opposite algebraic sign.

STRONG BASES

The dissociation constant of CaOH^+ has been determined by Davies & Hoyle (42) from the solubility of $\text{Ca}(\text{IO}_3)_2$ in aqueous solutions of $\text{Ca}(\text{OH})_2$. They estimate that, in a saturated solution of the latter (0.02 *M* $\text{Ca}(\text{OH})_2$), about 25 per cent of the calcium is present as CaOH^+ . The new value (0.05 $_0$) of the constant agrees well with the value (0.05 $_1$) determined by Bell & Prue (14) from kinetic measurements.

The dissociation constants of the hydroxides of metals have been compared by Davies (41) with the respective constants of various salts of the same cations. The comparative smallness of the dissociation constants of the hydroxides, he suggested, is due to the failure of the hydration shell to provide the protection which it usually offers to the metal cation. The paper contains a valuable summary of data. Some of the larger values ($K>0.1$) may prove eventually to be without significance either quantitative or qualitative.

STRONG ACIDS

The constitutions of pure sulfuric acid and of solutions of various solutes in it have been investigated by Gillespie *et al.* (72). They resolved conflicting reports in the literature and reported new cryoscopic measurements. In the pure acid two types of dissociation occur: "self-dehydration" (producing H_3O^+ and HS_2O_7^-) and "autoprotolysis" (producing H_2SO_4^+ and HSO_4^-).

[See also Reinhardt (199); Hammett (87).] Their investigations included solutes such as: acetone, acetic acid, SO_2Cl_2 , HSO_3Cl , N_2O_3 , N_2O_5 , HNO_3 , inorganic sulfates, and, especially, H_2O and SO_3 (oleums). The cryoscopic work was supplemented by Millen's (162) analyses of Raman spectra.

Using a photoelectric instrument for the determination of integrated intensities of Raman lines, Young, Maranville, and Smith (247) have determined the concentrations of the various molecular species in aqueous sulfuric acid as functions of the stoichiometric molarity, C . At 25°C ., the (SO_4^{2-}) reaches a maximum of 2 moles l^{-1} when $C=7$ moles l^{-1} ; it then decreases, becoming *ca.* zero when $C=15$ M . The (HSO_4^-) reaches a maximum of nearly 14 moles l^{-1} when $C=14$ and drops nearly to zero in an 18.6 M solution (pure acid). Undissociated H_2SO_4 was not detected in solutions in which C was less than 14 M .

Solutions of 75 to 80 organic solutes in absolute sulfuric acid have been studied cryoscopically, and by other methods [Szmant, Devlin & Brost (225, 226); Newman & Deno (173); O'Brien & Niemann (179)]. Brode & Wyman (24) have examined nine dyes in concentrated sulfuric acid.

Cryoscopic investigations of the constitutions of anhydrous nitric acid and of solutions of solutes in it have been reported by Dunning & Nutt (55) and Gillespie, Hughes & Ingold (73). Raman spectral studies were made by Ingold & Millen (108) and Goulden & Millen (78). [Cf. Redlich (198).] Raman spectra were employed also in an extensive study of mixtures of nitric acid and other strong acids [Ingold, Millen & Poole (109)].

WEAK ELECTROLYTES AND COMPLEX IONS

During 1951 more than 300 papers dealing with equilibria in solution and with the structure of solute molecules were published. For reasons stated elsewhere in this review, some of the results reported are erroneous, but limitations of space prohibit a critical evaluation of individual papers. The following brief references will illustrate current interest in the subject and demonstrate the variety and scope of current work. For other recent reviews see Bjerrum (17), Burkin (27), Fernelius (58), and Taube (227).

Consecutive equilibrium constants.—In 1914 Jaques (114) published a review of work on complex ions in aqueous solutions. In a brief appendix he discussed the investigation of equilibria existing simultaneously in the same solution. He considered particularly the formation of a series of complexes produced by the union of a positive ion with varying numbers of negative ions of a single species. He stated explicitly, however, that the method had "never been applied successfully."

In 1941 Bjerrum (16) reported his investigations of "consecutive equilibrium constants." He proposed that variations in activity coefficients be restrained by limitation of the concentrations of all reactants and products to ranges small in comparison with that of an inert electrolyte (often called the "neutral electrolyte" or "solvent electrolyte"). He was unable, in general, to determine true thermodynamic equilibrium constants because of de-

ficiencies in existing knowledge of activity coefficients. From the measurement of the concentration of one or another reactant or product, however, he could calculate the other concentrations involved and, from these, could determine a useful equilibrium quotient which varied with the nature and concentration of the neutral electrolyte but which was essentially constant so long as the nature and concentration of the neutral electrolyte was unchanged. Because of the upper limits placed on the concentrations of the reactants, the method could be applied to the study of firm complexes only, i.e., those whose dissociation quotients (and constants) are small.

Leden (130) attempted to study relatively unstable complexes by permitting the concentration of the reacting anion to increase to large values, comparable to those of the concentration of the neutral electrolyte. To restrain variations in the activity coefficients, he adjusted the concentration of the neutral salt to keep the total ionic strength, I , constant. Assuming negligible variations of activity coefficients, and negligible liquid-junction errors, he studied, for example, the reactions between Cd^{++} and SCN^- during a potentiometric titration of Cd^{++} with SCN^- . He equated the reciprocal of (Cd^{++}) to an empirical power series of (SCN^-) . From the respective empirical constants he determined equilibrium quotients for the series of reactions:



Since 1941 many other investigators have attempted to make similar determinations, frequently holding the volume ionic strength constant at values as large as 2 or 3 M .

Some authors, aware of variations in f 's when I is held constant, realized that those variations, if large, prevented determinations of thermodynamic constants but stated explicitly that quotients, nevertheless, could be determined. The statement is false. It is not the variation in f , which prevents the conversion of K' to K ; it is lack of information concerning absolute values of the coefficients. For the mere evaluation of a quotient, it is necessary that the f 's be constant or that their variations be known and provided for; otherwise, no significant thermodynamic function, whatever, is obtained.

Too little is known of the variation of f 's at constant I to permit reliable estimates of uncertainties from this source. Substitution of one univalent ion for another, e.g., Na^+ or H^+ for K^+ , or Cl^- for OH^- has been shown to produce changes in γ_{\pm}^2 of a uni-univalent electrolyte such as HCl or NaOH as large as 50 to 70 per cent when I is held at 2 or 3 M . [Cf. Harned & Owen (95) p. 454; Wahl & Bonner (237) p. 257.] Unfortunately even less is known of the effect of change of solvent electrolyte on f_{\pm} of electrolytes of higher charge types, e.g., $\text{Cd}(\text{SCN})_2$ or CdSCN^+ , especially when the ions interchanged bear a charge opposite in sign to that of the important multi-charged ion.

It is well known to those who have evaluated power-series equations

to represent experimental data that very small changes in the data often cause very large changes in the empirical factors of terms of order higher than the first. Variations in activity coefficients may cause such alterations; even orders of magnitude and algebraic signs of the factors may be altered.

Hume, DeFord & Cave (104) have reinvestigated the complexes of Cd^{++} and SCN^- . They used half-wave potentials observed during polarographic titration as a measure of the apparent concentration of Cd^{++} . Unfortunately, the ionic strength (2 instead of 3) and the solvent salt (KNO_3 instead of KClO_4) were not the same as those used by Leden. Nevertheless, the values of β_1 and β_2 agree fairly well with those determined by Leden (Table I). Note, however, that the observed values of β_3 differ by nearly two orders of magnitude and that the value reported for β_4 is the largest included in the 1951 paper, although Leden had concluded that it was negligible. Hume, DeFord & Cave blame these absurd discrepancies on the fact that they

TABLE I
STABILITY QUOTIENTS OF COMPLEXES OF Cd^{++} AND SCN^-

	Leden (25°C.)	Hume, DeFord & Cave (30°C.)
I	3.0	2.0
β_1	24.5	11 ± 0.5
β_2	96	56 ± 2
β_3	380	6 ± 5
β_4	—	60 ± 10

varied (SCN^-) over a wider range than Leden did. Regardless of the cause of the discrepancies, Table I illustrates the uncertainties which may exist when the ionic strength is high, even though it be held constant.

Since relatively small changes in concentrations can produce huge changes in calculated quotients, it is obvious that either relatively small experimental errors or reasonable—and not unexpected—variations in activity coefficients can change estimated quotients by several orders of magnitude. All of the determinations of equilibrium quotients after the first one or two in a series are to be regarded as suspect. The second quotient and even the first in some sets may prove to be greatly in error. We shall be fortunate if many more than half of the values determined by methods such as these should eventually prove to be significant. Doubtless many complexes reported will be found not to exist in appreciable amounts, and numerous others not reported will be shown to be important.

*Equilibria involving inorganic anions.*³—Scheffer & Hammaker (206)

³ The following symbols indicate methods used: [A], conductance; [θ], cryoscopy; [s], solubility; [Po], polarography; [pH], pH including electrometric titration; [e.m.f.],

found no complexes of fluoride with Cu(II), Co(II), or Ni(II) in 0.1 *M* solutions but have detected [OD; e.m.f.] MnF_6^{3-} and CrF^{++} . Dodgen & Rollefson (50) have determined [e.m.f.] quotients for the formation of FeF^{++} , FeF_2^+ , and FeF_3 from Fe^{3+} , and HF, and of ThF^{2+} , ThF_2^{++} , and ThF_3^+ from Th^{4+} and HF. The solubility of ThF_4 was also reported. Complexes formed by the reaction of Th^{4+} with HF have been investigated further [TTA] by Day & Stoughton (46) and Zebroski, Alter & Heumann (249). The results of their studies of solutions containing sodium perchlorate as a solvent electrolyte are in excellent agreement with those of Dodgen & Rollefson. Day & Stoughton extended their studies to solutions containing nitrate ion, instead of perchlorate ion. Preliminary values of the equilibrium quotients were 15 to 20 per cent larger. Assuming that the discrepancies were due to the formation of a mixed complex of Th^{4+} , F^- , and NO_3^- , they calculated an equilibrium quotient for its formation. On the other hand, the discrepancies may have been caused, as the authors recognized, by variations in activity coefficients. The question can not be resolved by conventional methods until more knowledge of activity coefficients of ions in mixtures has become available. The association of Ce^{3+} with F^- , Br^- , and I^- has been studied by Mayer & Schwartz (150). They reported [IER] formation quotients for CeF^{++} and CeBr^{++} , but detected no CeI^{++} . Rulfs & Elving (202) have found evidence [Po] for the combination of rhenide ion, Re^- , with F^- , Cl^- , Br^- , and I^- .

McConnell & Davidson (153) have investigated the absorption of light by solutions containing Cu(I), Cu(II), and HCl. Such solutions absorb much more light (λ between 400 and 600 $\text{m}\mu$) than is to be expected for simple mixtures of Cu(I) and Cu(II) salts. The effect, sometimes called "interaction absorption," has long been known. The increase in optical density was found to be proportional to the product of the concentrations of Cu(I) and Cu(II). According to McConnell & Davidson, Cu(I)Cu(II)Cl_2 is responsible for the increased absorption. Comparable increases in absorption were determined for solutions containing Sb(III) and Sb(V) by Whitney & Davidson (241); for Fe(II) and Fe(III) by McConnell & Davidson (154); for Sn(II) and Sn(IV) by Browne, Craig & Davidson (25). In each case the increase in optical density was found to be proportional to the product of the concentra-

e.m.f. of stable cells; [IER], ion exchange resin; [K], kinetics; [OD], optical density; [D], distribution between solvents; [TTA], distribution between an aqueous solution and a benzene solution of thenoyltrifluoroacetone, TTA.

The following abbreviations and symbols are used, as in current literature, to represent certain common substances: en, ethylenediamine (1,2-ethanediamine); pn, 1,3-diaminopropane; ptn, 1,2,3-triaminopropane; den, diethylenetriamine; trien, triethylenetetramine; tren, β, β', β'' -triaminotriethylamine; py, pyridine; dipy, α, α' -dipyridyl; *o*-phen, 1,10-phenanthroline (orthophenanthroline); oxine, 8-hydroxyquinoline (8-quinolinol); HPn, 2,4-pentanedione (acetylacetone); TTA, thenoyltrifluoroacetone; H_3X , nitrilotriacetic acid; H_4Y , ethylenediamine tetra-acetic acid (enta acid); H_2Bz^- , pyrocatechine-3,5-disulfonate (tiron); H_2Ch^- , 1,8-dihydroxynaphthalene-3,6-disulfonate (chromotropic acid); Cit^{3-} , citrate ion.

tions of the element in the two valence states. The constitutions of the respective complexes were not determined. The effect was not observed in solutions containing $Tl(I)$ and $Tl(III)$, $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, $Pd(II)$ and $Pd(IV)$, $Pd(II)$ and $Pt(IV)$, or $Pt(II)$ and $Pt(IV)$ [McConnell & Davidson (151); Ibers & Davidson (107); Cohen & Davidson (31)]. In general, the complexes did not seem to influence the rate of isotopic exchange. It is interesting to note, however, that irradiation with light of a frequency absorbed by the tin complex increases the rate of isotopic exchange between $Sn(II)$ and $Sn(IV)$ [Craig & Davidson (35)].

The equilibrium quotients obtained [OD] by McConnell & Davidson (152) for cupric chloride complexes are not in agreement with the observations [OD; s] of Näsänen & Lumme (169, 170). Näsänen & Lumme (170) have pointed out a credible reason for the discrepancy. The nature of the absorption spectra of cobaltous chloride solutions in water and organic solvents has been studied by Katzin & Gebert (120) and Dawson & Chaudet (45). James (113) has determined [A] a dissociation constant for the ion, $Co_2(trien)_3Cl^{6+}$, which exists in dilute solutions of $Co_2(trien)_3Cl_6$, a salt of the 6:1 charge type. Connick & Mayer (32) have estimated [IER] the formation quotient for $CeCl^{++}$. Schuffe, Stubbs & Witman (209) have reported [Po] complex ions of $In(III)$ with Cl^- . Both Day & Stoughton (46) and Zebroski, Alter & Heumann (249) have reported [TTA] formation quotients for complexes of Th^{4+} with Cl^- . The solutions employed in the two studies were of different ionic strengths; hence, the discrepancies between the results are not unexpected. Barney, Argersinger & Reynolds (7) have reported [s] the complex ion, $AgCl_2^-$. Hamm & Shull (86) have studied [Po] the rate of hydrolysis of $CrCl_2^+$. Alberty & King (3) have calculated formation quotients for four complexes of Cd^{++} with I^- from moving-boundary studies. Evidence for I^+ (solvated) in pyridine [OD] was presented by Zingaro, VanderWerf & Kleinberg (250) and in H_2O [e.m.f.] by Bell & Gelles (13). Greenwood & Emeléus (80) investigated the dissociation of liquid ICl .

Using, as a titrating agent, ammonium paramolybdate which presumably replaces each molecule of water of hydration in Cr^{3+} with $HMoO_4^-$, Hall & Eyring (85) obtained evidence for the formation of polynuclear ions containing $Cr(III)$ joined by oxygen bridges. Bawn & White (12) have suggested similar ions in solutions containing $Co(III)$ to explain the rate of decomposition of water by cobaltic sulfate and perchlorate. Studying the hydrolysis of Fe^{3+} in aqueous solutions of $Fe_2(SO_4)_3$ and H_2SO_4 , Arden (4) noticed [A; pH] that a slow change takes place over a period of months. Siddall & Vosburgh (219) observed [OD] that the slow change occurs in solutions prepared by dilution of concentrated solutions, but not in those prepared directly from a solid salt, and have suggested that the change is due to the slow decomposition of some polynuclear species containing the $Fe(III)$. The discrepancy between the values reported by Siddall & Vosburgh and by Arden for the formation of $FeOH^{++}$ may be due to Arden's neglect of activity coefficients. In investigations [OD; A; pH] of the hydrolysis of Ti^{3+} ,

Hartmann & Schl fer (96) postulated the existence of polynuclear species of Ti(III). The observations of Tewari & Ghosh (230) on the precipitation of aluminum hydroxide are consistent with the existence of an aluminate polymer discussed by Jahr & Plaetschke (111). Connick & Reas (33) have proposed that perchloric acid solutions of Zr(IV) contain "polymers" having the formula, $(\text{Zr}(\text{OH})_2 \cdot \text{XH}_2\text{O})_n^{n+}$ in which n may be large. The method of calculation makes heavy demands upon the data [TTA]. Confirmation by other methods is desirable. Using the Debye-H ckel approximation to estimate activity coefficients, Kraus & Nelson (128, 172) have obtained [OD; pH; Po] equilibrium constants for the hydrolysis of U(IV), the disproportionation of U(V) to U(IV) and U(VI), and the formation of UCl^{3+} and UO_2Cl^+ . Their value for the hydrolysis quotient of Pu^{4+} agrees satisfactorily with that reported [e.m.f.] by Rabideau & Lemons (197). Hardwick & Robertson (88) have determined [OD] equilibrium quotients for the hydrolysis of Ce^{4+} and the formation of dinucleic species of Ce(IV).

A study [A] of $\text{Co}(\text{NO}_3)_2$ in acetophenone by Stern & Templeton (221) corroborates the evidence [OD] of Katzin & Gebert (120) for a disproportionation reaction of $\text{Co}(\text{NO}_3)_2$ in organic solvents. Nayar & Pande (171) have found indications [A] of complexes in solutions of $\text{Pb}(\text{NO}_3)_2$. Glueckauf, McKay & Mathieson (74, 158) have shown [A] that the dissociation of $\text{UO}_2(\text{NO}_3)_2$ is small in esters, ethers, and ketones, but much larger in alcohols. Proportionality was observed between the concentrations of water and the salt in all organic solvents investigated except alcohols. The lack of proportionality in alcohols is in agreement with the results [D] of Templeton & Daly (229). Formation quotients for CeNO_3^{++} and CeSO_4^+ were reported [IER] by Connick & Mayer (32) and for PuNO_3^{3+} and PuSO_4^{++} [e.m.f.], by Rabideau & Lemons (197). Both determinations were based upon the assumption that f_{\pm} is affected only by ionic strength. Because of the difference between the ionic strengths of the solutions studied [TTA] by Day & Stoughton (46) and by Zebroski, Alter & Heumann (149), the values reported for the formation quotients of ThNO_3^{3+} do not agree quantitatively.

Zebroski, Alter & Heumann (249) investigated also the formation of ThSO_4^{++} , $\text{Th}(\text{SO}_4)_2$ and $\text{Th}(\text{HSO}_4)(\text{SO}_4)^+$. James (113) has shown [A] that the ion $\text{Co}_2(\text{trien})_3^{6+}$ is largely associated with SO_4^- even in dilute solutions. Ahrlund (2) has reported [pH; OD] approximate values for the formation quotients of five complexes of UO_2^{++} with SO_4^- and acetate ion.

Jahn & Staude (110) have determined [s; e.m.f.] equilibrium quotients and ΔF° , ΔH° and ΔS° for the formation of $\text{Ag}(\text{SO}_3)_2^{3-}$ at temperatures from 2° to 50°C. Unfortunately, they neglected variations in activity coefficients even when the ionic strength was altered.

Furman & Garner (70) have shown [OD] that $\text{V}(\text{SCN})^{++}$ and $\text{VO}(\text{SCN})^+$ exist. Investigating [OD] solutions of $\text{Co}(\text{SCN})_2$ in *t*-butanol and isopropanol, Katzin & Gebert (121) reported the existence of $\text{Co}(\text{SCN})_2$ and $\text{Co}(\text{SCN})_3^-$. West & de Vries (240), on the other hand, concluded that [OD]

Co(SCN)^+ and Co(SCN)_6^{4-} are present in H_2O and H_2O -ethanol mixtures. Further work is desirable.

From ebulliometric determinations, Mitchell & Macdonald (163) have shown that ferric thiocyanate in moist ether, and in alcohol solutions, exists as Fe(SCN)_3 rather than $\text{Fe}_2(\text{SCN})_6$. Macdonald, Mitchell & Mitchell (142) have obtained [OD; D] formation quotients for the complexes, $\text{Fe(SCN)}_n^{(3-n)+}$. Their observation that the quotient for the formation of Fe(SCN)^{++} depends upon the salt used as solvent electrolyte is obviously the result of the variability of activity coefficients at constant ionic strength.

Equilibria involving organic anions.—Lloyd, Wycherley & Monk (139) found [s] that the dissociation quotients of complexes of Cu^{++} with a large number of monocarboxylate ions exhibit the same relative variations as do the dissociation constants of the respective acids. A similar parallelism was observed [TTA] by Day & Stoughton (46) between the constants of mono-, di-, and trichloroacetic acids, and the corresponding complexes of Th^{4+} . Davies & Monk (44) concluded [s] that both dielectric constant and solvent-ion interaction are important factors affecting the dissociation constant of silver acetate in the mixed solvents—water plus methanol, ethanol, glycol, glycerol, acetone and dioxane. Similar effects were observed by Monk (166) for the solubilities of AgBrO_3 , $\text{Ca(IO}_3)_2$, $\text{Ba(IO}_3)_2$, and $\text{La(IO}_3)_3$ in the same solvents. Peterson & Dienes (186) estimated [s] the dissociation quotient for $\text{Ag(C}_2\text{H}_3\text{O}_2)_2^-$ in acetic acid. Fronaeus (62) determined [IER] stability quotients for three complexes of Cu^{++} with acetate ion. He showed that the values are in good agreement with his previous estimates [e.m.f.]. This agreement indicates only that the experimental methods were applied correctly, not that the assumptions underlying the calculation of the quotients were valid. Ahrlund (1) determined [pH; OD] the formation quotients of three complexes of UO_2^{++} with acetate ion. Barney, Argersinger & Reynolds (7) reported [s] dissociation quotients for $\text{Mg(C}_2\text{O}_4)_2^{2-}$, $\text{Ni(C}_2\text{O}_4)_2^{2-}$, $\text{Cd(C}_2\text{O}_4)_2^{2-}$, and $\text{Co(C}_2\text{O}_4)_2^{2-}$. Crouthamel & Martin (38) measured [s] dissociation constants of the first two complexes and estimated that of the third complex of oxalate ion with each of the following: Ce^{3+} , Nd^{3+} and Yb^{3+} . Nydahl (178) pointed out that the divergence between the observed and calculated solubilities of $\text{Ca(C}_2\text{O}_4)_2$ in solutions containing oxalate ion indicates complex formation. The stability constants of the complexes of Ba^{++} , Cu^{++} , La^{3+} , and $\text{Co(NH}_3)_6^{3+}$ with anions of several dicarboxylic acids were measured [pH; Λ] by Peacock & James (184). It was shown [OD; Po] by Pecsok (185) that $\text{Ti(C}_2\text{O}_4)_2^-$ and $\text{TiO(C}_2\text{O}_4)_2^-$ are the important oxalate complexes of titanium and that the stability constant is greater for the Ti(IV) than for the Ti(III) complex. Feldman, Neuman, Danley & Havill (57) used dialysis to ascertain that the ratio of Be(II) to citrate is 2:1 in the complex which is predominant in solutions of beryllium citrate. Meites (161) reported [Po] estimates of equilibrium constants for reactions involving CuCit^- , CdCit^- , ZnCit^- , and FeCit which are not self-consistent. The neglect of complexes

containing two anions of citric acid may be responsible for some of the difficulty.

Meek & Banks (160) have determined [OD] the dissociation constant of the complex ion, $\text{Be}(\text{sulfosalicylate})_2^{4-}$, by an extrapolation of the quotients obtained at various ionic strengths. Monk (164) estimated [s; pH] dissociation constants of complexes of Ag^+ , Cu^{++} , Pb^{++} , Zn^{++} , Ni^{++} , Co^{++} , Mn^{++} , Mg^{++} , and Ca^{++} with anions of glycine, alanine, and glycyl-glycine. Monk (165) reported [s] that the dissociation constants of the complexes of anions of amino acids with Ca^{++} , Ba^{++} , and La^{3+} agree more closely with the Kirkwood than with the Scatchard treatment of ion-dipole interaction. Buser (28) presented evidence [IER] for complexes produced by the reactions of Na^+ and Li^+ with uramil-diacetic acid. Maschka & Bogner (146) found indications [Λ ; θ] of complexes of Na^+ with aniline, pyridine and dimethylamine. Schwarzenbach and his co-workers made extensive investigations [pH] of the formation of complexes of Mn^{++} , Fe^{++} , Fe^{3+} , Co^{++} , Ni^{++} , Cu^{++} , Zn^{++} , Cd^{++} , Hg^{++} , Ag^+ , Pb^{++} , and La^{3+} with ethylenediamine tetraacetate ion (212, 213), nitrilotriacetate ion (211, 214), and several polyamines (194, 195, 210). Schwarzenbach & Freitag (212) suggested that the discrepancies between their determinations of the relative stabilities of the complexes of Cu^{++} , Ni^{++} , Pb^{++} , and Co^{++} with ethylenediamine tetraacetate ion and those reported [OD] by Plumb, Martell & Bersworth (191) are due, at least in part, to failure of those workers to consider the presence of the buffer in their solutions. The stability quotients of complexes of Cd^{++} with diethylenetriamine and triethylenetetramine reported [Po] by Douglas, Laitinen & Bailar (52) differ considerably from estimates made by Prue & Schwarzenbach (195, 210). Jonassen, LeBlanc & Rogan (116) reported [pH] stability quotients for complexes of Ni^{++} and Cu^{++} with diethylenetriamine which differ but slightly from those of Prue & Schwarzenbach despite differences in experimental conditions. Excellent agreement exists between values of the formation quotients of the 1:1 complexes of Ni^{++} and Cu^{++} with triethylenetetramine obtained [pH] by Jonassen & Meibohm (117) and Schwarzenbach (210). Jonassen & Meibohm reported that the presence of $\text{Ni}_2(\text{trien})_2^{4+}$ is consistent with their measurements [pH], but apparently did not consider $\text{Ni}(\text{Htrien})^{3+}$ for which Schwarzenbach gave a stability constant (210). Block & Bailar (18) reported a polyamine complex of a different type. It arose from the dissociation of one hydrogen ion from an amino group in $\text{Au}(\text{en})_2^{3+}$. Linhard & Weigel (138) studied the absorption spectra of $\text{Co}(\text{NH}_3)_5\text{X}^{++}$ and $\text{Cr}(\text{NH}_3)_5\text{X}^{++}$ (X^- denotes a halide ion) and estimated the stability quotient of $(\text{Co}(\text{NH}_3)_5\text{F})\text{I}^+$. Phillips and associates (187, 188, 189) determined [OD] the compositions and solubilities of complexes of Fe^{3+} , Cu^{++} , and Zn^{++} with 8-quinolinol and some of its derivatives. Unfortunately, their attempts to determine relative stabilities of the complexes were based upon the unjustified assumption that the most stable complexes are the least soluble. Cartledge (30) measured [OD] equilibrium quotients

for the dissociation of Mn(Pn)_2 to Pn^- and Mn(Pn)_2^+ and for the hydrolysis of the latter ion. From estimates [OD] of the formation quotients of complexes of Zr^{4+} with the anion of chloranilic acid, Thamer & Voigt (231) concluded that Zr^{4+} is not appreciably hydrolysed in 1 and 2 *M* perchloric acid solutions. Dorta-Schaeppi, Hürzeler & Treadwell (51) estimated [OD] equilibrium quotients for the reactions of alizarin with Al^{3+} , Ti^{4+} , Zr^{4+} , Sn^{4+} , Hf^{4+} , and Th^{4+} . Harvey & Manning (97) have used the reactions of Fe^{3+} with "tiron" to illustrate several methods [OD] for the determination of the composition of a complex. None of the methods appear to have revealed the dissociation observed [OD] by Schwarzenbach & Willi (215) of Fe(HBz) to yield Fe(Bz)^- and H^+ . Heller & Schwarzenbach (102) reported [OD, pH] stability quotients of the complexes formed by reaction of Fe^{3+} with chromotropic acid. Duke & Bremer (53) estimated [K] the hydrolysis quotient of Ce^{4+} and the equilibrium quotients for the reactions of Ce^{4+} with 2,3-butanediol.

Dissociation of weak acids.—Bates (8) examined the utility of buffered concentration cells (without liquid-junctions) of the type used by Harned and his co-workers for investigations of ionic equilibria. He proposed a procedure (9) to be used for the study of acids whose dissociation constants are 10^{-3} or somewhat larger. His method utilizes concentration cells for the determination of the product of the dissociation constant of the relatively strong acid and the dissociation constant (already known) of a weaker acid. Using acetic acid as the weaker electrolyte, he determined the equilibrium constant for the dissociation of formic acid.

Buffered concentration cells without liquid junctions were studied over a temperature range to determine ΔF° and other thermodynamic quantities; e.g., ΔH° , ΔS° and ΔC_p° , for the dissociation of the following: D-tartaric acid by Bates & Canham (10), monoethanolammonium ion by Bates & Pinching (11), sulfanilic acid by MacLaren & Swinehart (144), β -alanine in water and water-isopropyl alcohol mixtures by May & Felsing (147), meta- and para-substituted benzoic acids by Briegleb & Bieber (23) and glycine in aqueous sodium chloride solutions by King (123). Using a differential potentiometric method, Grunwald & Berkowitz (83, 84) measured the dissociation constants of formic, acetic, and benzoic acids in water-ethanol mixtures. To correlate dissociation constants of several acids in a number of solvents and to facilitate predictions, they tabulated values of two parameters, one determined by the nature of the solvent and the other by the structure of the acid.

In an investigation of the effects of substituents upon the basicity of naphthylamine, Bryson (26) determined [pH] acid dissociation constants of the conjugate acids of some substituted naphthylamines. An investigation [pH] of the effect of organic silicon substituents on the basic strength of methylamine was made by Noll, Daubert & Speier (176). Values of equilibrium constants were reported for the first acid dissociation [pH; OD] of

5- and 6-ammoniumquinolinium ions by Hearn, Morton & Simpson (101); for the first and second dissociation [pH; s] of *p*-diethylammoniumbenzylidenerhodanine ion by Sandell & Neumayer (204); and for the first and second dissociations [pH; OD] of the conjugate acids of some para-substituted *p'*-dimethylammoniumazobenzene ions in aqueous sulfuric acid and ethanol solutions, respectively, by Rogers, Campbell & Maatman (201). Tucker & Irvin (232) obtained [pH; OD] values of the first and second dissociation constants of 4-hydroxyquinolinium ion and of the dissociation constants of the conjugate acids of 4-methoxyquinoline and N-methyl-4-quinolone. From these values, they estimated the equilibrium constant for the lactam-lactim tautomerism of 4-hydroxyquinoline. From studies of conductance, viscosity, and electrolysis, Greenwood, Martin & Emeléus (81, 82) concluded that $\text{BF}_3 \cdot \text{CH}_3\text{COOH}$, $\text{BF}_3 \cdot \text{H}_2\text{O}$ and $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ in their liquid states are strong acids and are largely dissociated. Stetten (222) reported evidence [pH] of polymeric molecules in aqueous solutions of boric acid.

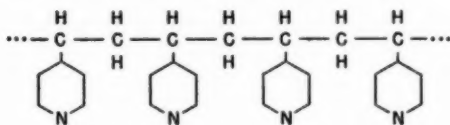
Lemaire & Lucas (131) used acid-base indicators and the acidity function, H_0 , of Hammett [(87) p. 267] in the determination of the basicity of acetonitrile, dioxane, *p*-toluenesulfonamide, water, acetanilide, acetamide, and urea (in the order of increasing basicity). A new acidity function, J_0 (related to H_0), was proposed by Gold & Hawes (75) who used it to determine the equilibrium constant for the reaction of H_2SO_4 with trinitrophenylcarbinol to yield HSO_4^- and a carbonium ion.

Equilibria of a new kind were studied by Förster (60). β -Naphthol and some of its derivatives in acid solutions possess fluorescence bands which are distinct from those of the same substances in less acidic or alkaline solutions. From measurements of pH and intensity of fluorescence, Förster estimated the quotient for the dissociation of each acid when both the acid and its anion are in excited states. Certain pyrene derivatives were similarly examined (59).

POLYELECTROLYTES

The subject of polyelectrolytes belongs as much to polymer chemistry, colloid chemistry, and biochemistry as it does to "Solutions of Electrolytes." Several recent papers should be described here, however, because they were written by investigators whose point of view was largely that of the student of electrolytic solutions. They worked with polyelectrolytes, not primarily to increase understanding of polymers, colloids, and proteins, but rather to increase understanding of interionic and intermolecular forces in general. Some common, naturally-occurring polyelectrolytes are proteins, polysaccharides, and nucleic acids. Familiar synthetic polyelectrolytes include polyvinylpyridinium salts and the salts of polyacrylic acid.

Fuoss and his co-workers studied polyelectrolytes, such as derivatives of poly(4-vinylpyridine),



A molecule of poly(4-vinylpyridine) itself is electrically neutral. Any one of the nitrogen atoms, however, may be converted to a quaternary atom; it may, for example, be allowed to react with a molecule of methyl bromide. The derivative so formed may exist as a bromide ion and a large positively charged polymeric ion; it is a strong electrolyte. The statistical configuration of a large molecule of poly(4-vinylpyridine) is presumably that of an open flexible coil. If many of the nitrogen atoms in the molecule have reacted with HCl or methyl bromide, multiple dissociation can produce a very highly charged coil and, thereby, large repulsive forces between adjacent parts of the coil. The coil accordingly expands [Fuoss & Maclay (68); Fuoss & Edelson (65)]. Addition of a simple electrolyte, e.g., NaBr, increases the concentration of negative ions within the coil, thus reducing the repulsive forces and causing the coil to contract. Conversely, the molecule uncoils and its configuration becomes more and more rod-like as a solution of the poly-electrolyte is diluted because dilution increases the probability of escape of the anion from the polymer molecule. These changes of shape account for characteristic variations of viscosity and other properties with concentration of this polymer or of the added electrolyte. This "picture" has been confirmed by studies of streaming birefringence in aqueous solutions of poly (4-vinyl-*n*-butylpyridinium) bromide [Fuoss & Signer (69)] and of light scattering [Fuoss & Edelson (66)].

Copolymers of maleic acid and styrene were studied by Garrett & Guile (71) who seem to have observed effects of electrostatic shielding by phenyl groups. According to Kuhn, Hargitay, Katchalsky & Eisenberg (129), undissociated polyacrylic acid is coiled into a ball-like mass. As the acid is neutralized, accumulating negative charges repel each other and the molecule becomes more rod-like. A theory of "the potential of an infinite rod-like molecule and of the distribution of the counter ions" has been developed by Fuoss, Katchalsky & Lifson (67).

Proteins.—Increased availability of homogeneous crystalline proteins during the last five years has made possible similar studies of the interactions of proteins with small ions. Complexes formed by the union of a variety of ions with the protein molecule have been investigated. Many of the observed phenomena have been explained in terms of electrostatic forces [Klotz, Walker & Pivan (127) and Scatchard, Scheinberg & Armstrong (205)], but not all [Karush (118)]. Measurements of temperature coefficients of equilibrium constants reveal that some, at least, of the heats of reaction

are small. Hence, entropy changes are dominant in these phenomena [Klotz (126)].

IRREVERSIBLE PROCESSES

DIFFUSION COEFFICIENTS

The availability of a precision technique for the measurement of differential diffusion coefficients has enabled Harned and his co-workers to investigate electrolytes of five charge types. Dilute aqueous solutions of the following salts seem to agree with, or differ but slightly from the theory of Onsager & Fuoss (181): LiCl, NaCl, AgNO₃ [Harned & Hildreth (92)]; Li₂SO₄, Cs₂SO₄ [Harned & Blake (89, 91)]; KNO₃, K₄Fe(CN)₆ [Harned & Hudson (93)]. The differential diffusion coefficient of Na₂SO₄ is only slightly larger, and that of LaCl₃ only a little smaller, than theory predicts [Harned & Blake (89, 90)]. The differential diffusion coefficients of ZnSO₄ and MgSO₄, on the other hand, are considerably larger than the values calculated from the theory [Harned & Hudson (94)]. Accepting the degrees of dissociation estimated by Owen & Gurry (183), Harned & Hudson calculated a constant related to the diffusion coefficient of each neutral ion pair in solutions of ZnSO₄ and MgSO₄.

Integral and differential diffusion coefficients of NaI and KI have been reported for a wide concentration range by Dunlop & Stokes (54), who used magnetically stirred, porous-diaphragm cells [Stokes (223)]. Self-diffusion of ions was discussed by Gosting & Harned (77). They concluded that attempts to measure ionic diffusion coefficients by radioactive tracer methods have been only partially successful. Values for highly dilute solutions seem to be incorrect. Self-diffusion in pure water has been studied by Wang using both deuterium (238) and O¹⁸ (239) as "tracers." He concluded that his results support the theory of a quasicrystalline structure of liquid water but that water at room temperatures is "only slightly more than two-coordinated."

CONDUCTANCE

Transference numbers in an anhydrous solvent have been measured precisely for the first time. Using a moving boundary method, Davies, Kay & Gordon (43) determined transference numbers for NaCl and KCl in anhydrous methanol. Butler, Schiff & Gordon (29) contributed conductance data needed for the determination of Λ_0 of each ion. Data for dilute solutions ($N < 0.002$) obey the Onsager-Shedlovsky equation. Baker & Kraus (6) examined the variation of Λ_0' [defined by Shedlovsky (217)] with decreasing concentration. They reported minima in the $\Lambda_0' - \sqrt{C}$ curves for aqueous solutions of several salts which obey the "extended Onsager equation" precisely.

Alkyl-substituted ammonium salts have been the subjects of several studies; they can be tailor-made for investigations of the effects of various factors, e.g., size, shape, symmetry. Working with symmetrical salts of vari-

ous molecular weights, Daggett, Bair & Kraus (39) found that the conductivities of all conform closely to the Onsager equation. The product $\Lambda_0\eta$ (η = viscosity) varies more from salt to salt in water than in other solvents. Comparing new measurements of conductivities of several salts in acetone with conductivities of salts in several other solvents, McDowell & Kraus (157) found that differences in macroscopic properties such as viscosity, density, and dielectric constant were not sufficient to account for variations in the conductivities of solutions of salts in those solvents. They suggested that hydrogen bonding may contribute to some ion-solvent interactions, e.g., between NH_4^+ and pyridine, and may supplement coulombic forces in the formation of ion pairs and other aggregates. Compelling evidence for valence forces much larger than coulombic forces was obtained by Lichtin & Bartlett (135) and Lichtin & Glazer (136) in their studies of the conductances of solutions of derivatives of triphenylmethyl chloride in sulfur dioxide.

Healey & Martell (100) compared the solvents, ethylene chloride and ethylidene chloride. The dielectric constants are nearly equal; so also are the products, $\Lambda_0\eta$, for each of about ten ions in the two solvents. The dissociation constants of ion pairs in ethylene chloride, however, are much larger than in ethylidene chloride. An explanation was proposed by Stern, Healey & Martell (220). Copenhafer & Kraus (34) used cryoscopic measurements to show that several salts in benzene exhibit marked association, but that ion-solvent interaction is virtually negligible. The solubilities of tetraethylammonium chloride in mixtures of benzene and ethylene chloride were measured by Vernon, Goldberg & LaRochelle (236). Solubilities of several quaternary ammonium salts in methanol-benzene mixtures were determined by Goldberg & Vernon (76). A marked anomaly in the solubility curve for tetraethylammonium iodide is ascribed tentatively to ion-solvent interaction.

Van Dyke, Crawford & Harrison (233, 234, 235) measured conductivities of solutions of AlBr_3 and AlCl_3 in nitrobenzene (or benzonitrile) each containing a small amount of one of the following: methanol, dimethyl ether, acetone, acetic anhydride, pyridine, and trimethylamine. The data indicate the existence of compounds formed by the reactions of the organic substances with the aluminum halides.

Long-chain electrolytes.—Kraus and his co-workers have replaced one methyl group in tetramethylammonium salts with normal alkyl chains, containing n carbon atoms [Bair & Kraus (5); McDowell & Kraus (155)]. When n is 10 or less, $\Lambda_0\eta$ of a long-chain salt in aqueous solution does not differ greatly from $\Lambda_0\eta$ of the symmetrical salt of the same molecular weight. The difference is larger when n exceeds 10. The trend of Λ_0 with n changes abruptly between $n=14$ and 16. The variation of Λ with \sqrt{C} (when C is less than the critical concentration) agrees with the Onsager theory for $n < 16$. For $n=16$ and 18, the Λ - \sqrt{C} slope is nearly twice the theoretical. The authors suggest that the steeper slope is due, not to association of ions whose charges are of opposite sign, but to interaction between the long-chain portions of ions of the same kind. Aqueous solutions of other, more complex

long-chain trialkylammonium salts have been studied by McDowell & Kraus (156). When the concentrations of the solutions are increased beyond their respective critical concentrations, the equivalent conductances change abruptly and, for several salts, exhibit maxima. The association of the ions of the long-chain salts in benzene was studied cryoscopically by Copenhafer & Kraus (34) and by Young & Kraus (246). "Association numbers" as large as 30 and 40 were reported and discussed, in conjunction with conductivity and polar moment data, as consequences of association. The importance of ion size and shape was also recognized. Somewhat similar work was done with long-chain ammonium sulfamates and long-chain pyridonium sulfamates in water and in a water-acetone mixture by Taylor, Desch & Catotti (228). There are maxima in the $\Lambda\text{-}\sqrt{C}$ curves of all (four) of the salts dissolved in the water-acetone mixture.

Bolaform electrolytes.—The form of an ion consisting of two quaternary ammonium groups connected by a chain several atoms in length resembles the shape of a bola, a missile weapon. The study of ions containing chains of several lengths was initiated by Fuoss & Edelson (64) and Fuoss & Chu (63). Variations, with increasing chain length, of the observed constants for the association of anions with divalent cations are small. One objective of the research is an understanding of monatomic ions bearing two charges, e.g., Ca^{++} .

THERMODYNAMIC PROPERTIES

ACTIVITIES AND ACTIVITY COEFFICIENTS

The stoichiometric mean activity coefficient, γ_{\pm} , of the ions of hydrochloric acid in aqueous solutions containing 5 and 10 per cent D-fructose was determined by Crockford & Sakhnovsky (36) from the e.m.f.'s of cells-without-liquid-junctions. They found that, for concentrations less than 0.12 molal, the Debye-Hückel approximation may be used to calculate γ_{\pm} for HCl satisfactorily if a value of 6.6 Å is used for the ionic parameter, a [(95) p. 37 *et seq.*]. This value for a is the same as that found by Williams, Knight & Crockford (242) for HCl in D-glucose solutions of the same concentrations. (The value of a for HCl in water is 4.3 Å.) Nicholson & Felsing (175) corrected their values of γ_{\pm} (for an error in calculation) of the perchlorates of Ca, Ba, Sr, and Mg, determined from cryoscopic data (174). From solubility measurements, Hayes & Martin (98) obtained γ_{\pm} for $\text{Mn}(\text{IO}_4)_2$ in sodium chloride solutions. Schubert (208) used a cation exchange resin to determine γ_{\pm} of barium nitrate (in "tracer" concentrations; ca. 10^{-6} molal) in aqueous solutions of uranyl nitrate as concentrated as 0.5 molal. Connick & Mayer (32) used the same technique to determine γ_{\pm} of cerous salts in aqueous solutions, 10^{-3} to 10^{-4} molal, containing mineral acids. Schmid, Maschka & Breit (207) determined γ_{\pm} of HCl in aqueous H_2SO_4 solutions. Using sodium and potassium amalgam electrodes, Sedlet & De Vries (216) determined γ_{\pm} of NaCl and KCl in liquid ammonia solutions at -36°C . The

activity coefficients deviate from the Debye-Hückel limiting law more rapidly than those of the same salts in water. The authors fitted the equation of Stokes & Robinson (224) to their data for NaCl, taking the ionic parameter, a , and the solvation number, n , to be 3.53 Å and 2.5, respectively. (The values for NaCl in water are 3.97 Å and 3.5.) For concentrations below 1 molal, Robinson, McCoach & Lim (200) fitted the equation of Stokes & Robinson to the values of γ_{\pm} of CoBr₂ and CoI₂ obtained isopiastically. The values of a and n are 5.35 Å and 16 for CoBr₂ and 5.93 Å and 20 for CoI₂.

Salting effects on nonelectrolytes.—If a nonelectrolyte is dissolved in a solvent whose dielectric constant is greater than that of the nonelectrolyte, addition of a strong salt usually causes a salting-out, i.e., an increase in the activity coefficient of the nonelectrolyte. According to simple electrostatic theories (those based upon coulombic forces alone), salting-out should always occur under these circumstances. Nevertheless, salting-in is sometimes observed, especially when the molecule of the nonelectrolyte and the ions of the electrolyte are all large. This phenomenon has been called "lyotropic salting-in" by Bockris, Bowler-Reed & Kitchener (20) who studied the salting-in of benzoic acid by tetra-alkylammonium iodides in water and in ethylene glycol solutions. By considering both "coulombic and dispersion ion-molecule interactions," they were able to develop a theory in, at least, qualitative agreement with their observations. Similarly, Long, McDevit & Dunkle (140, 141) obtained an empirical equation involving polarizibilities of the ions and the ionic strength which fits their observations of the effects of alkali halides upon (a) the activity coefficient of γ -butyrolactone, (b) the equilibrium constant for the hydrolysis of the lactone to γ -hydroxybutyric acid and (c) the rate of the reaction. Heal (99) reported accurate measurements of changes in the solubility of ether in water produced by addition of ammonium nitrate, certain tetralkylammonium nitrates and nitrates of the alkali and alkaline earth metals.

IONIC ENTROPIES

The standard partial molal entropies, S° , of monatomic ions in aqueous solution have been compiled by Powell & Latimer (193). They found close agreement with a simple semi-empirical function of the atomic weight, M , the absolute value of the ionic charge, z , and the ionic radius, r , from crystal dimensions, thus:

$$S^\circ = (3/2)R \ln M + 37 - 270z/(r + p). \quad 9.$$

The parameter p is 2.00 Å for anions and 1.00 Å for cations. The equation is not in accord with the Born (22) electrostatic model.

SOLVATION

Bockris (19) suggested division of the total solvation number into two parts: "primary" and "secondary." The primary solvation number is the

number of solvent molecules which, together with an ion, constitute a mechanical unit that moves during electrolytic transport as a single entity. The solvent molecules in the unit have lost their own translational degrees of freedom. "Secondary solvation" refers to all "electrostatic interactions which are not included" in the primary solvation. [Cf. Samoilov (203).]

Determination of the relative masses of ions by the method suggested in 1933 by Debye (47) is not yet feasible. Progress has been reported, however, in the measurement of ultrasonic vibration potentials. Yeager, Bugosh & Hovorka (245) detected the effect in dilute aqueous solutions. Its amplitude was nearly independent of concentration of the electrolyte, but varied from electrolyte to electrolyte.

Hydration of the periodate ion IO_4^- was investigated by Crouthamel, Hayes & Martin (37). They measured optical density in a study of the acid dissociation of the molecular species: H_5IO_6 , H_4IO_6^- , and $\text{H}_3\text{IO}_6^{2-}$. Certain variations in the optical density seem not to be associated with acid-base reactions but with the equilibrium,



If their interpretation is correct, H_4IO_6^- predominates in aqueous solutions at room temperature. Above 70°C . and in solutions in which the mole fraction of water has been reduced by a mixture with methanol, the species IO_4^- predominates.

Using an isotopic tracer technique, Hunt & Taube (105) demonstrated that no less than six molecules of water are held by each Cr^{3+} ion. The water is held so firmly that the half-time for exchange of water containing O^{18} with ordinary water is more than 40 hr. They studied also the thermodynamics of the isotopic distribution showing that the proportion of H_2O^{18} in the hydration water is slightly greater than in the bulk water when equilibrium has been reached.

The method has yielded no information concerning other similar ions studied (Co^{++} , Co^{3+} , Al^{3+} , Ga^{3+} , Th^{4+} , and Fe^{3+}), presumably because any exchange which occurred was essentially complete within 3 min. [Friedman, Taube & Hunt (61); Hunt & Taube (106)]. The method may not be useful for more than two or three simple aqueous ions but will probably illuminate the constitutions of ions of more complicated types. If improvements in technique should permit measurement after shorter intervals (less than 3 min.), the method may become capable of detecting primary hydration numbers of ions not now amenable to study.

Among the simplest spectra of ions in solution are those of the monatomic halide ions. Several attempts have been made to explain them, but success has been limited. Platzman & Franck (190) have been able to show that certain older theories of the absorption process are untenable. They cite their own photochemical investigations of the production of elementary iodine and elementary hydrogen by irradiation of oxygen-free solutions of iodides

in water. They observed an absolute quantum efficiency nearly proportional to hydrogen ion concentration when the concentrations were small, but approaching a limit of about unity as acid concentrations were increased. They concluded that a back reaction destroys the effects of the primary absorption act except when a hydrogen ion is able to accept an electron before the energy is dissipated as heat.

Platzman & Franck proposed that the absorption act is the transfer of an electron from the negative halide ion to the sheath of water molecules adjacent to the ion. The transfer is so quick that the water molecules do not have time to rearrange themselves. By virtue of their orientation they create an attractive field for the electron and hence reduce the energy required for transfer. Utilizing this model the authors were able to calculate the frequency of the longer wave length bands of the halide ions without arbitrary assumptions and with a precision better than was anticipated.

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REACTION KINETICS¹

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Since scientific papers which could be catalogued as reaction kinetics are currently being published at a rate of more than a thousand per year, a simple bibliography of one year's publications would fill the space allotted this review. Fortunately for the reviewer, many papers fall into special fields such as photochemistry, polymerization, contact catalysis, isotopic studies, or biochemical kinetics, which will be reviewed separately in the present volume or succeeding volumes of the *Annual Review of Physical Chemistry*. The present review then can be limited to the more conventional gas-phase and solution reactions.

During 1951 one textbook on reaction kinetics has appeared: Hougen's *Reaction Kinetics in Chemical Engineering* (1). This short monograph (74 pages) presents in printed form a lecture on chemical kinetics as applied to process design, originally given at the 43rd Annual Meeting of the American Institute of Chemical Engineers, in December, 1950.

From the myriad experimental techniques used in reaction rate studies, we may single out for special mention those which have been useful for very fast reactions. The rapid photometric technique for the study of gas reactions, described by Johnston & Yost (2), is being used by both of them. Wayne & Yost (3) have studied the reaction of N_2O_3 with H_2O in the gas phase, and have found it to be first-order with respect to N_2O_3 and second-order with respect to H_2O . Johnston and co-workers have studied a number of gas reactions; one example is the reaction of NO with O_2 , for which Johnston & Slentz (4) obtain rates in good agreement with earlier workers. Chance (5) has described instrumentation for rapid spectrophotometry. McKinney & Kilpatrick (6) have developed a high speed strain gauge manometer for following fast pressure changes. Burrell, Majury & Melville (7) have studied polymerization reactions with a dielectric constant method which uses a frequency of 50 Mc. and has a time resolution of 10^{-3} sec. Axmann (8) also has used a dielectric constant method to follow reactions in solution. Most of the investigators of very fast reactions have used oscilloscopic display for time measurement. It may be remarked in passing that the measurement of short time intervals is not a significant difficulty in these investigations; the circuitry now in use by nuclear physicists for rapid differential counting permits a time resolution of 10^{-9} or 10^{-10} sec.

GAS REACTIONS

Bond dissociation energies.—Chiefly with the aid of reaction kinetic data, a systematic thermochemistry of free radicals is being built up. To Szwarc's

¹ The survey of the literature pertaining to this review was concluded in December, 1951.

important review of the subject (9) he has published an addendum (10) which brings his tabulation up to date, and in fact includes the results of a considerable amount of unpublished work by himself and Leigh. Table I

TABLE I
CARBON-HYDROGEN BOND DISSOCIATION ENERGIES

$\text{CH}_3\text{—H}$	101–102 kcal.
$\text{C}_2\text{H}_5\text{—H}$	96–97
<i>iso</i> - $\text{C}_3\text{H}_7\text{—H}$	ca. 94
<i>tert</i> - $\text{C}_4\text{H}_9\text{—H}$	ca. 88
<i>n</i> - $\text{C}_3\text{H}_7\text{—H}$	99 ?
<i>n</i> - $\text{C}_4\text{H}_9\text{—H}$	101 ?
$\text{C}_6\text{H}_5\text{CH}_2\text{—H}$	77.5
$(\text{C}_6\text{H}_5)(\text{CH}_3)\text{CH—H}$	ca. 74
$(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{C—H}$	ca. 71
$(\text{C}_6\text{H}_5)_2\text{CH—H}$	ca. 72

lists some carbon-hydrogen bond dissociation energies for which new data have been obtained. The value cited for the $\text{CH}_3\text{—H}$ bond energy is still that of Kistiakowsky & Van Artsdalen (11). The pyrolysis of nitromethane,



looks like a good reaction from which to find the heat of formation of methyl radical. The pyrolysis of it and of other nitroalkanes has been studied by three groups of investigators (12, 13, 14), who find that the reaction yields a complex mixture of products, that the apparent activation energy varies with initial pressure, and that the reaction is not strictly first-order. Consequently, the apparent activation energy, which is somewhat lower than expected for reaction 1, need not in fact be ascribed to reaction 1.

The figure given for C_2H_5 is based on the pyrolysis of propylbenzene, for *n*- C_3H_7 of *n*-butylbenzene, for $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{CH}$ of isopropylbenzene, and for $(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{C}$ of *tert*-butylbenzene, all unpublished data of Leigh and Szwarc. The figures for isopropyl, *tert*-butyl, *n*-propyl and *n*-butyl are from electron impact data on hydrocarbons, by Stevenson (15). The agreement between the results obtained by the pyrolytic method and the appearance potential method is excellent. The bond dissociation energy for the benzyl-hydrogen bond is partly based on the pyrolysis of dibenzyl, for which Horrex & Miles (16) find the first-order rate constant $10^{9.3} e^{-48,000/RT}$ sec.⁻¹; this result is somewhat doubtful because of the anomalously low frequency factor. The energy for the diphenylmethyl-hydrogen bond is obtained from Horrex & McCrae's pyrolysis of diphenylmethane (17), for which they find the first-order constant $10^{13} e^{-73,000/RT}$ sec.⁻¹.

The carbon-bromine bond dissociation energies have been determined by the toluene-carrier pyrolysis technique, for substituted bromomethanes by Sehon & Szwarc (18), and for substituted benzyl bromides by Leigh, Sehon

& Szwarc (19). Szwarc (20) has demonstrated the usefulness of his tables by using them to predict the course of formation of olefines from hydrocarbon radicals.

Frequency factors of unimolecular reactions.—Szwarc (21) has tabulated the frequency factors for a number of unimolecular decompositions which are now thought to be free from side reactions. The frequency factors lie between 10^{12} and 10^{15} sec.⁻¹, or, in the language of absolute reaction rate theory, the entropies of activation lie between 0 and +15 e.u. The surprising feature is not that some activation entropies are as high as +15 e.u., but that some are as low as zero; for, as Rice (22) has pointed out, "if two of the atoms in a molecule are widely separated, as they are in the activated complex, other frequencies also would be greatly loosened."

The pyrolysis of acetic anhydride in the temperature range 280–650°C. has been studied by Szwarc & Murawski (23). The reaction is



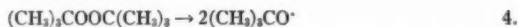
The reaction is nonradical, since the pyrolysis in the presence of toluene yields no dibenzyl. The first-order rate constant is $10^{13.0} e^{-34,500/RT}$ sec.⁻¹.

The pyrolysis of isopropyl bromide, by Maccoll & Thomas (24),



adds another to the already considerable list of alkyl halides which decompose by a nonchain mechanism. The addition of propylene, bromine, or allyl bromide does not affect the initial rate. At large conversions, however, the back reaction of HBr with propylene must be taken into account. The reaction is first order over a pressure range of 30–450 mm. Hg, the rate constant being $10^{13.6} e^{-47,800/RT}$ sec.⁻¹. The pyrolyses of propyl chloride and of butyl chloride are likewise reported to be nonchain, by Barton, Head & Williams (25). The reactions have no induction period and are unaffected by propylene. Their respective first-order constants are $10^{13.4} e^{-55,000/RT}$ sec.⁻¹ and $10^{14.0} e^{-57,000}$ sec.⁻¹. On the other hand, the pyrolysis of dichlorodiethyl ether is a chain reaction with a chain length of about 23. So also is the pyrolysis of tetrachloroethane (26), with a chain length of about 500.

The thermal decomposition of di-*tert*-butyl peroxide has been reinvestigated by Murawski, Roberts & Szwarc (27). Both static and flow techniques were used, and toluene was added to some reaction mixtures but not to others. The reaction was studied over a temperature range of 120° to 280°C. The rate constant obtained for the reaction



is $10^{14.7} e^{-36,000/RT}$ sec.⁻¹, which fits satisfactorily not only the authors' data but also those of Raley, Rust & Vaughan (28).

Quasi-unimolecular reactions.—Undoubtedly the definitive work on the decomposition of N_2O_5 in the presence of NO is that by Johnston and co-workers (29, 30; see also 31). The rate measured is that of the reaction



5.

which is involved also in other reactions of N_2O_5 (32). The reaction was studied over a total pressure range of more than 10^4 -fold: from 0.05 mm. to 7000 mm. Hg. Both the high-pressure first-order limit and the low-pressure second-order limit of the quasi-unimolecular reaction have been approached. The authors have interpreted their data in terms of the Rice-Ramsperger-Kassel theory (33).

Johnston (34) has also re-examined the existing data on the decomposition of N_2O , and has pointed out that after these have been corrected for a heterogeneous reaction which becomes important at low pressures, most of the scatter of the data disappears. After this correction has been made, the data for the N_2O decomposition agree satisfactorily with the Rice-Ramsperger-Kassel theory.

Frequency factors of bimolecular reactions.—Steacie & Szwarc have published a note (35) deprecating the use of the term "normal steric factor" in the discussion of bimolecular reactions, since some authors mean by this that the steric factor is practically unity while others mean that it is in accord with calculations based on the transition-state theory. Observed frequency factors range from about $10^{9.5}$ to $10^{5.5}$ $\text{sec}^{-1} \text{ atm}^{-1}$, decreasing with increasing complexity of the radicals involved. The higher value represents approximately a steric factor of unity, so steric factors as small as 10^{-4} are not unexpected. Among the bimolecular gas reactions reported in 1951, almost this full range of frequency factors is illustrated.

The highest is that for the recombination of methyl radicals,



6.

reported by Gomer & Kistiakowsky (36). The bimolecular constant for this reaction is $10^{9.1} e^{-(0 \pm 700)/RT}$ $\text{sec}^{-1} \text{ atm}^{-1}$. It was determined by the intermittent-light technique in the photolysis of acetone and of mercury dimethyl. It is of particular importance that this rate constant be known accurately, because it can then be used as a reference value to obtain the reaction rates of CH_3 radicals with other substrates.

It is interesting to recall that Gorin, in 1938, worked out the application of the absolute reaction rate theory to the recombination of free radicals, and obtained (37)

$$k_2 = 12^{1/2} \pi^{1/2} \Gamma(2/3) p_0 (kT)^{-5/6} \alpha^{2/3} I^{1/3} m^{-1/2} \quad 7.$$

p_0 being the number of dynes cm^{-2} in 1 atm., α the polarizability of the methyl radical, I its ionization potential, and m its mass. On insertion of the proper numerical values, we obtain for the recombination rate the value $k_2 = 10^{9.7}$ $\text{sec}^{-1} \text{ atm}^{-1}$. The close agreement of Gorin's theory is possibly fortuitous, but his general picture that the methyl groups in the activated complex are far apart, so that its entropy is unusually high, cannot be far wrong.

Several bimolecular gas reactions have been reported this year whose fre-

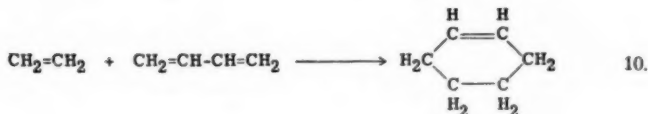
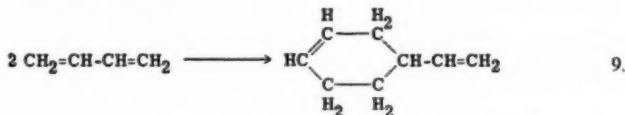
quency factors are approximately $10^{7.5}$ sec. $^{-1}$ atm. $^{-1}$. Johnston & Crosby (38) have investigated the bimolecular reaction of NO with O_3 , at -43° and -75°C ., and have given the second-order rate constant as $10^{7.3} e^{-2100/RT}$ sec. $^{-1}$ atm. $^{-1}$. Blades & Winkler (39), using nitrogen atoms produced by the discharge technique, have studied the reaction of N atoms with CH_4 at $300\text{--}450^\circ\text{C}$.; the second-order constant is $10^{7.4} e^{-11,000/RT}$ sec. $^{-1}$ atm. $^{-1}$. Miller & Steacie (40), making use of methyl radicals produced photochemically, have measured the rate of the reaction of CH_3 with NO, as compared with the recombination rate of methyl radicals. If we accept Gomer & Kistiakowsky's value for the recombination rate, the rate for the bimolecular reaction of methyl radicals with nitric oxide, which presumably has no activation energy, is $10^{7.3}$ sec. $^{-1}$ atm. $^{-1}$. Among the older reactions having nearly this frequency factor are the reaction of Br atoms with CH_4 , for which $A = 10^{7.6}$ sec. $^{-1}$ atm. $^{-1}$, reported by Kistiakowsky & Van Artsdalen (11); the reaction of NO_2 with O_3 , for which $A = 10^{7.4}$ sec. $^{-1}$ atm. $^{-1}$, reported by Johnston & Yost (2); and the reaction of O_2 with HBr, for which $A = 10^{7.6}$ sec. $^{-1}$ atm. $^{-1}$, reported by Szabo & Kiss (41).

Trotman-Dickenson & Steacie (42) have carried out an extensive investigation of the reaction



using methyl radicals produced by photolysis of acetone or mercury dimethyl. They have studied 35 compounds, including normal and branched alkanes, cycloalkanes, alkenes, alkynes, benzene and toluene, ethers, acetone, alcohols and amines. The frequency factors for their reactions are closely bunched around a single value, half of them falling within $10^{6.0 \pm 0.3}$, and all but four within $10^{6.0 \pm 0.6}$ sec. $^{-1}$ atm. $^{-1}$. (For compounds containing two or more reactive hydrogens, the rate constant per hydrogen atom is used in the calculation.) Gomer & Kistiakowsky's value for the rate of methyl radical recombination has been used in the computation of the rate constants. In terms of the transition-state theory, the observed frequency factor corresponds to an entropy of activation for the reaction of -33.8 ± 2 e.u., which is very nearly the translational entropy of a methyl radical.

Rowley & Steiner (43) have extended the investigation of the two gas-phase diene addition reactions,



finding for reaction 9 in the high-temperature region (600°C.) the rate constant $10^{6.1} e^{-26,800/RT}$, and for reaction 10, $10^{5.7} e^{-27,600/RT}$ sec.⁻¹ atm.⁻¹. Carrington & Davidson (44) have measured the dissociation rate of N₂O₄ by fast photometric technique, after raising the temperature of the reaction mixture suddenly by passing a shock wave through it. They find at 25°C. a first-order rate constant of 1×10^5 sec.⁻¹. Inasmuch as the equilibrium constant for the association is 7 atm.⁻¹ at 25°C., the rate constant for the association reaction



is $10^{5.85}$ sec.⁻¹ atm.⁻¹. Since the reaction probably has no activation energy, this figure is probably the frequency factor. Marcotte & Noyes (45), using photochemically produced methyl radicals, have studied the reaction



and have found that the activation energy is near zero, and the frequency factor is $10^{9.5}$ sec.⁻¹ atm.⁻¹, which is rather surprisingly low.

Activation energies for hydrogen abstraction.—The activation energies for the reactions of CH₃ radicals with hydrocarbons, studied by Trotman-Dickenson & Steacie (42), fall in the range 7 to 11 kcal. For primary hydrogens the activation energy is 9.5–10.5 kcal., for secondary hydrogens about 8.5 kcal., and for tertiary hydrogens about 7.5 kcal. There is a parallel trend of these activation energies with the corresponding bond strengths, the variation in activation energies being roughly one-half that in the bond strengths (46). However, the markedly weaker bonds of toluene and of propylene (see Table I) have activation energies for the methyl radical reaction of 8.3 kcal. and 7.7 kcal. respectively, so the parallel cannot be pushed too far.

The rates of reaction of H atoms with a number of hydrocarbons have been reported by Schiff & Steacie (47). They find the order of reactivity to be the same toward H atoms as toward methyl radicals. Anderson, Davison & Burton (48) find the activation energy for the reaction



to be 4.6 kcal. higher than that for acetone, or 6.2 kcal. higher than that for acetaldehyde. Accordingly, the activation energy for reaction 13 is some 13.2 to 13.7 kcal. The activation energy for D₂ is some 1.1 kcal. higher yet.

Kooyman (49) has studied the liquid-phase abstraction of hydrogens from various α -methylene compounds by CCl₃ radicals. He finds the same order of reactivity that Gregg & Mayo (50) did for chain transfer in styrene polymerization. Kharasch & Buchi (51) have made a qualitative study of the reactivity of various chloro-alkanes in solution with the radicals from the decomposition of acetyl peroxide. They find the order of decreasing reactivity to be *tert*-H, *sec*-H with Cl, *sec*-H, *pri*-Cl and *sec*-Cl, *tert*-Cl and *pri*-H.

Miscellaneous pyrolyses.—The pyrolysis of diborane has been subjected to thorough investigation by Clarke & Pease (52) and by Bragg, McCarty &

Norton (53). The reaction is of $3/2$ order, its rate constant being $10^{11.4} e^{-28,000/RT}$ sec. $^{-1}$ atm. $^{-1/2}$. Mass spectrographic analysis of the reaction mixtures shows that the initial product of the reaction is exclusively B_3H_{11} ; B_5H_9 begins to appear after a substantial time lag, presumably as a secondary product from the B_3H_{11} . The reaction exhibits a small but definite inhibition by added hydrogen. A reaction sequence consistent with these observations is the following:



Reaction 14, followed by a rapid reaction of BH_3 with D_2 , has been invoked by Maybury & Koski (54) to explain their finding that the deuterium exchange with diborane is $3/2$ order with respect to the diborane, but independent of the deuterium.

Ingold, Stubbs & Hinshelwood (55) have continued their study of the pyrolysis of hydrocarbons in the presence of nitric oxide, which they regard as a unimolecular, nonchain process. However, there is room to doubt that NO really suppresses the chain reaction, since the composition of pyrolysis products is the same in the presence as in the absence of NO, and since the authors find that the addition of NO sometimes (as with propylene) produces an actual increase of the rate. It would be desirable to have a demonstration that the reaction is in fact nonchain, as by the pyrolysis of a mixture of deuterated and nondeuterated hydrocarbon, with mass spectrographic analysis of the pyrolysis products. This is the technique which has been used for the study of the pyrolysis of ethane by Wall & Moore (56), and for the pyrolysis of acetaldehyde by Wall & Moore (57) and Zemaný & Burton (58). For both reactions, the isotopic mixing is extensive, which shows that under the conditions of the experiments the pyrolyses proceed principally (though possibly not exclusively) by chain mechanisms.

Walters and his co-workers have examined the pyrolysis of cyclobutane (59), which appears to yield ethylene by a homogeneous, nonchain path; and of dioxolane (60), ethylene oxide (61), and tetrahydrofuran (62), all of which are markedly affected by ethylene and may be presumed to be chain reactions. The thermal decomposition of HNO_3 was found by Johnston *et al.* (63) to be chiefly heterogeneous, though a homogeneous reaction of high activation energy supervened at temperatures above 400°C . Under the experimental conditions used by Hanratty *et al.* (64) the decomposition of N_2H_4 was wholly heterogeneous. Partington & Neville (65) found the decomposition of CSO (to CO_2 and CS_2) to be catalyzed by silica at low temperatures, but were able to measure its homogeneous first-order decomposition at 550 – 600°C . The pyrolysis of S_2F_{10} (to SF_6 and SF_4) was found by Trost & McIntosh (66) to be partly heterogeneous, to be accelerated by addition of nitric oxide or dichloroethylene, and to have a very high apparent frequency

factor (about 10^{19} sec.⁻¹), all of which betray the chain nature of the reaction.

COMBUSTION AND AUTOXIDATION

The major publication of the year in the field of combustion was the new edition of Lewis & von Elbe's *Combustion, Flames and Explosions of Gases* (67). Like the authors' 1938 monograph of the same name, this is an indispensable reference work to any investigator in the field. During the year, two symposia pertinent to the field have appeared: one on Combustion Chemistry, printed in the December issue of *Industrial & Engineering Chemistry*, and the other the *Discussions of the Faraday Society*, No. 10, on Hydrocarbons. Reference to particular papers from these symposia will be made here as the topic comes up for discussion.

From studies on the explosion limits for H_2-O_2 mixtures in B_2O_3 -coated vessels, Egerton & Warren have proposed (68), and Broida has confirmed (69), that these walls are far less destructive to H atoms than are KCl-coated walls. They propose that the second-order chain branching reaction



17.

becomes operative in the boric acid-coated vessels. Broida & Oldenberg (70) have extended to lower temperatures the second explosion limit for H_2-O_2 , and have confirmed the applicability of Lewis & von Elbe's theory, wherein the chain is propagated in the gas phase and terminated at the surface. The nonexplosive reaction between N_2H_4 and O_2 has been investigated by Bowen & Birley (71), using a static method. The initial rate is approximately first order with respect to each reactant. The data do not permit a very accurate computation of the activation energy or frequency factor for the reaction. Since the rate is considerably reduced by packing the vessel, and since the addition of propylene or ethylene reduces the rate to about 15 per cent of its former value, the authors conclude that the reaction is a chain of five or six steps, terminating on the walls. Murray & Hall (72) have reported flame speeds for hydrazine-oxygen mixtures. Price (73) has determined the low-pressure explosion limits for pentaborane-oxygen mixtures.

The oxidation of solid metals by oxygen gas is being investigated by a number of workers. The amount of activity in this field can be appreciated by listing the metals for which oxidation studies were reported during 1951: As (74), C (75), Ca (76), Co (77, 78), Cu (79), Fe (80), Ge (81), Ni (77, 78), Si (82), Th (83), and Zn (84, 85).

Flame propagation.—A large fraction of the papers on flames have to do with their technological aspects, or with their spectroscopic or hydrodynamic properties, so are not of direct concern to chemical kineticists. In this category, for example, is the paper by Hirschfelder & Curtiss (86), which is a continuation of the authors' comprehensive mathematical study of the theory of flame propagation. So also is the contribution by Karlovitz,

Denniston & Wells (87), in which they have related turbulent flame velocity to laminar flame velocity, and have shown the necessity of taking into account the turbulence resulting from the flame itself.

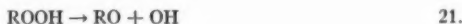
Simon (88) has examined the flame speed data for 56 hydrocarbons, including the data of Gerstein, Levine & Wong (89) and also unpublished data by the investigators at Experiment, Inc. She finds that these data are in good agreement with the Pease-Tanford (90) theory of flame propagation, which is based on the hypothesis that the reaction rate in the flame zone is first order with respect to various active species such as H, OH, and O, the concentrations of which are governed by upstream diffusion from the burned gases. The Pease-Tanford equation is

$$U^2 = \frac{LQ}{Q'} \sum \frac{k_i D_i p_i}{B_i} \quad 18.$$

where U is the flame velocity, L the molecules per cubic centimeter of gas at the flame temperature, Q the mole fraction of potential combustion product, Q' the mole fraction of combustible, k the rate constant for the reaction of combustible with an active particle, D the diffusion coefficient for the active particle, p the equilibrium partial pressure of the active particle, and B a term near unity arising from recombination of active particles. For any particular combustion mixture, all the parameters except the rate constant k can be computed a priori, so that a measurement of flame velocity is tantamount to a measurement of this rate constant. For the flames studied by Simon, the average rate constant is $0.75 \times 10^6 \text{ sec.}^{-1} \text{ atm.}^{-1}$, or $1.4 \times 10^{11} \text{ sec.}^{-1} \text{ mole}^{-1} \text{ cc.}$

Another test of the Pease-Tanford theory has been reported by Friedman & Burke (91), who have studied the flame speeds of acetylene and deuterioacetylene with air. From their data they calculate the ratio of rate constants $k_{C_2H_2}/k_{C_2D_2}$ to be 0.92, which is in agreement with theoretical expectation.

Hydrocarbon oxidation.—There is wide agreement that the oxidation of hydrocarbons proceeds through peroxidic intermediates, according to a scheme more or less like that presented by Bell and co-workers (92):



It has been the authors' program to obtain direct chemical evidence for each of the individual reactions. Reaction 19, the uptake of oxygen by an alkyl radical, has been demonstrated by Marcotti & Noyes (45) using photochemically produced methyl radicals, and by Raley *et al.* (93) using methyl radicals from the pyrolysis of *tert*-butyl peroxide.

Reactions 20 to 24 provide three independent paths by which RO_2 radicals can be converted into RO radicals. An example of reaction 20, hydroperoxide formation, is found in the gas-phase oxidation of isobutane, with HBr as the hydrogen donor (94). The reverse reaction has been detected in the pyrolysis of *tert*-butyl deuteroperoxide (95), by the formation of deuteromethane. Reaction 21, the unimolecular fission of the hydroperoxide, has been studied quantitatively for *tert*-butyl hydroperoxide in liquid *n*-octane (92); however, the reaction is a combination of a unimolecular and a chain process. Reaction 22, the bimolecular formation of dialkyl peroxide, was demonstrated (95) by the isolation of ethyl *tert*-butyl peroxide from the pyrolysis of a mixture of *tert*-butyl hydroperoxide and di-*tert*-amyl peroxide. Reaction 23, fission of the dialkyl peroxide, has now been demonstrated in a number of hydrogen-donating solvents (96). The bimolecular oxygen-forming reaction 24 has been inferred by the authors from their work with methyl radicals (93). However, the same conclusion could have been drawn from the earlier work by Milas & Surgenor (97), who decomposed *tert*-butyl hydroperoxide to obtain an almost quantitative yield of O_2 and *tert*-butyl alcohol, presumably by way of reaction 24 and the reverse of 20.

According to reactions 25 and 26, the ultimate fate of an alkoxy radical is either to pick up a hydrogen to yield the alcohol, or to split off an alkyl (or hydrogen) group to become a ketone (or aldehyde). The relative importance of these two modes of decomposition has been assessed by Rust *et al.* (98) for six different alkoxy radicals in liquid cyclohexene.

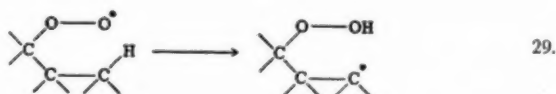
Bateman *et al.* (99) have studied the liquid phase oxidation of ethyl linoleate and four other olefinic compounds, initiated by azo-bis-isobutyronitrile. They assume the Bolland mechanism, which comprises as chain-propagating steps reactions 19 and 20, and as chain-terminating steps 22, 27, and 28:



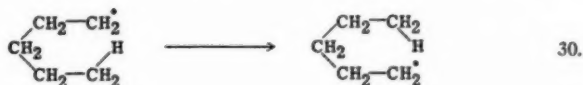
From the effect of oxygen on the rate, and by making use of the nonstationary rate of photochemical oxidation, they are able to compute the five rate constants separately. Mulcahy (100) has worked out the kinetic consequences of the Bolland mechanism for the oxidation of gaseous hydrocarbons at low temperatures.

Organic compounds for which gas-phase oxidation rates and product compositions have been reported this year include methane (101, 102), propane (103), methyl ethyl ketone (104), methylamine (105), methyl cyclo-

pentane (106), *n*-heptane and methylcyclohexane (107). Thomas & Crandall (108), in the course of an ultraviolet spectrophotometric study of the pre-flame combustion of butane and pentane, have identified in the products the beta-dicarbonyl compounds, butanal-3-one from butane and 2,4-pentanedione from pentane. They propose for a mechanism an internal hydrogen abstraction by the peroxy radical:



This intramolecular reaction is reminiscent of the internal hydrogen abstraction by the alkyl radical, assumed by Voge & Good (109) to explain the product composition in the thermal cracking of higher paraffins:



The most recent review of the subject of autoxidation is by Frank (110). Ingraham & Corse (111) have reported that the autoxidation of chlorogenic acid, which is involved in the "browning" of vegetables, is first order with respect to each reactant and inversely proportional to the H^+ concentration. Mulcahy & Watt (112) have investigated the peroxide-induced autoxidation of benzaldehyde. Cooper & Melville (113) have used the intermittent-light technique to obtain the chain length for the autoxidation of *n*-decanal.

Wibaut & Strang (114) have used cobalt stearate to catalyze the autoxidation of alkanes; they report the rates for nine *n*-alkanes, seven branched alkanes, and three cycloalkanes. From the oxidation of 2,5-dimethylhexane they have isolated the corresponding 2,5-dihydroperoxide. Brook & Matthews (115) have used copper stearate and ferric stearate to catalyze the autoxidation of liquid lubricating oil. Bawn, Pennington & Tipper (116) have studied the rate of autoxidation of 2-methyl-butene-2 catalyzed by soluble cobalt salts. They find the steady state concentration of hydroperoxide to be proportional to $(\text{RH})^2$, and the rate of O_2 uptake to be proportional to $(\text{Cat})^{1/2}(\text{RH})^2$; they have not found a reaction scheme which is consistent with both these observations.

Bawn & Williamson (117) have shown that the cobalt catalyzed autoxidation of acetaldehyde in solution proceeds in two distinct steps: (a) the catalyzed oxidation of acetaldehyde to peroxyacetic acid, and (b) the catalyzed decomposition of a 1:1 compound of acetaldehyde and peroxyacetic acid, to yield acetic acid and acetic anhydride. The rate of step (a) is proportional to the aldehyde and the cobaltous concentrations, but independent of

oxygen pressure. The reaction shows an initial auto-acceleration, which is eliminated by the addition of peroxyacetic acid. The mechanism proposed is: a chain initiated by the reaction of cobaltic ion with peroxyacetic acid, and terminated by the reaction of peroxyacetyl radical with peroxyacetic acid. The equilibrium constant for the formation of the complex (presumably hydroxyethyl acetyl peroxide) in step (b) has been measured, and the rate of its decomposition has been found to be roughly proportional to the cobaltous salt present.

Other reactions of organic peroxides.—Since organic peroxides arise commonly in autoxidations, it will be appropriate to collect here some of their reactions which have been studied this year. Friess & Soloway (118) have made a kinetic study of the reaction of peroxyacid with various substituted acetophenones. Since, however, some of their reactions followed a first-order and some a second-order course, the meaning of the relative rates listed by them is somewhat obscure. The subject of peroxyacids was reviewed by Swern (119) in 1949.

The acid-catalyzed cleavage of a hydroperoxide, to yield the corresponding ketone and the alcohol of the group split off, is known for many hydroperoxides. A kinetic study has been made by Witkop & Patrick (120) of this cleavage reaction for 11-hydroperoxy-tetrahydrocarbazolenine. The decomposition rate of acetyl peroxide in dimethylphthalate, acetic acid, and CCl_4 has been measured by Ross & Fineman (121), and that of *tert*-butyl peroxybenzoate in 12 solvents by Blomquist & Ferris (122). The curious decomposition of di-hydroxymethyl peroxide,



which is formed reversibly from formaldehyde and H_2O_2 , has been investigated kinetically by Dunicz, Perrin & Style (123) and by Jaillet & Ouellet (124). The reaction is first order and independent of acidity, its rate constant being $10^{12.9} e^{-26,100/RT} \text{ sec}^{-1}$.

Bawn & Mellish (125) have followed the decomposition of benzoyl peroxide in solution by measuring the uptake of the stable, highly colored free radical, diphenyl-picryl-hydrazyl—the Bartlett & Kwart (126) technique. They find the first-order rate constant in benzene to be $10^{13.5} e^{-26,600/RT} \text{ sec}^{-1}$. [They have also measured the decomposition rate of azo-bis-isobutyronitrile. For other work on the azo-bis-nitriles, see (127) and (128).] The same technique has been used by Chapiro (129) and by Matheson *et al.* (130).

MEDIUM EFFECTS

The question of medium effects in the liquid phase and, in particular, the question of the Brønsted-Debye-Hückel theory of salt effects were discussed in the Symposium on Anomalies in Reaction Kinetics (131). Bell *et al.* (132) have repeated Liebhaftsky & Mohammad's (133) old work which purported to find no salt effect in the third-order reaction of iodide with peroxide; the present authors do find a salt effect in agreement with that expected from the

Brønsted theory. Long, McDevit & Dunkle (134) have studied the kinetics of the hydrolysis of butyrolactone, including salt effects, and have also measured the activity coefficient of the lactone in various salt solutions. The magnitude of the salt effect on the neutral molecule (which is usually imagined to be negligible) is easily enough to account for the variation in the observed rate constant.

Olson, Frashier & Spieth (135) have studied the racemization of dimethyl-*l*-bromosuccinate by LiBr in acetone. The authors have chosen to describe their data by the empirical equation

$$k = \frac{k_1(\text{Br}^-) + k_2(\text{LiBr})}{[1 + k_3(\text{ester})][1 + k_4(\text{ClO}_4^-)]} \quad 32.$$

Ciappetta & Tomlinson (136), investigating the reaction between bromoacetate and thiosulfate in aqueous propyl alcohol, have shown that the rate exhibits a strong maximum at a concentration of added La^{+3} corresponding to the stoichiometric formation of LaS_2O_3^+ , and have inferred that this species is one of the actual reactants. The correctness of this hypothesis is confirmed by the observation (137) that the reaction in water as well as in the aqueous alcohol can be described by a reaction scheme which includes LaS_2O_3^+ as a reactant with bromoacetate; and, moreover, that this contribution to the rate shows a salt effect as expected from the Brønsted-Debye-Hückel theory.

The need to take into account, in any kinetic study, the formation of weak electrolytes or complex ions has been further indicated by the work of Hodgson, Evans & Winkler (138) on the exchange of radio- I^- with *n*-butyl iodide in acetonitrile, which shows LiI, NaI, and CsI to be strong electrolytes in this solvent but ZnI_2 , CdI_2 , and I_2 to be weak. Also, Bell & Waind (139) have used the kinetics of nitramide decomposition in the presence of the salts of weak acids, as a tool for the determination of their dissociation constants. They have obtained values for calcium, barium, and zinc complexes of mandelate, salicylate, malate, and fumarate.

Heyding & Winkler (140) have found that an increase of dielectric constant gives a decrease in the rate of exchange of radio- I^- with *n*-butyl iodide, as expected for the reaction of an ion with a neutral molecule. The effect of solvent on the solvolysis of organic halides and tosylates has been reviewed by Winstein, Grunwald & Jones (141), from the point of view of mechanism (formation or nonformation of covalent bond to the solvent), and the correlation of rates with the Winstein-Grunwald "Y-function" (142). In the limiting mechanism wherein no covalent bond is formed to solvent, the solvolysis rate k in a particular solvent is related to the rate k_0 in a reference solvent (80 per cent ethanol) by the relation

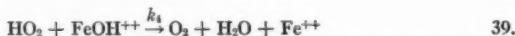
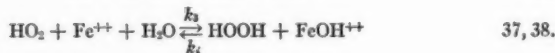
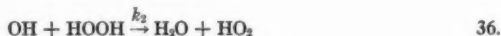
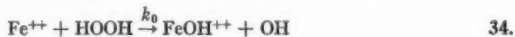
$$\log (k/k_0) = mY \quad 33.$$

where m is a parameter characteristic of the reaction, Y one characteristic of the particular solvent.

The Hammett H_0 -function, which extends the pH scale to high acidities, has proved useful in the study of several acid-catalyzed reactions reported this year: the hydrolysis of butyrolactone (134), the decarbonylation of benzoylformic acid (143) and the racemization of alkyl bisulfates (144). Harbottle (145) has tabulated the H_0 -function for perchloric acid. The acid-catalyzed hydrolysis of benzophenone ethyl acetal has been examined by Andrews & Kaeding (146) in aqueous ethanol mixtures. As the solvent composition is changed, the rate passes through a minimum; this is another good example of the effect of mixed solvents on the acidity function. Levy *et al.* (147) have reported a careful study of the rate of hydration of isobutene in the presence of HNO_3 . In 0.973 M acid the entropy of activation is -27.3 e.u., and in 0.0909 M acid it is -31.2 e.u., the difference between the two values being approximately the entropy calculated for dilution of the acid. Barham & Clark (148) state that the rate of decarbonylation of nearly anhydrous formic acid is inversely proportional to its water content; it is likely that this dependence is caused by the variation of acidity function with water content.

INORGANIC REACTIONS IN SOLUTION

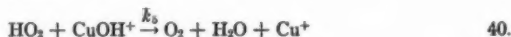
What is probably the definitive kinetic study on the reaction of H_2O_2 with ferrous and ferric ions has been published by Barb, Baxendale, George & Hargrave (149). The reaction scheme they propose is essentially²



By suitable variation of the experimental conditions, the authors have been able to isolate various of these steps for separate study. At high concentrations of Fe^{++} or H^+ , reaction 39 is negligible, so reaction 34 can be studied. Its rate constant is $k_0 = (kT/h) e^{19/R} e^{-8800/RT} \text{ sec}^{-1} \text{ mole}^{-1} \text{ l}$. In the presence of added Fe^{+++} or Cu^{++} or both, reaction 37 is negligible, so the ratio k_2/k_1 can be found; it is approximately 10^{-1} at both 0°C . and 25°C . At a high ratio of H_2O_2 to Fe^{++} , reaction 35 is negligible, so that the ratio k_4/k_3 can be evalu-

² The reviewer has taken the liberty of writing reactions 38 and 39 in the form given, involving the species FeOH^{++} , which is consistent with the dependence of these reactions on the acidity. The current literature offers many other examples of ionic reactions in which the reactive species appears to be the hydrolyzed, rather than the simple metallic ion. The authors have preferred to write the same reactions in terms of Fe^{+++} and HO_2^- , and Fe^{+++} and O_2^- , respectively.

ated; its value, based on FeOH^{++} , is about 1.3. From the reaction of Fe^{+++} with peroxide at a high ratio of peroxide to ferric, reaction 38 can be studied. Its rate constant at 25°C ., based on FeOH^{++} , is $2.3 \times 10^{-4} \text{ sec}^{-1} \text{ mole}^{-1} \text{ l}$. In addition, the authors have found that cupric ion is even more effective than ferric in the oxidation of HO_2 ,



and have evaluated the ratio k_3/k_2 .

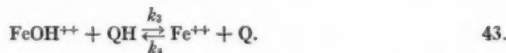
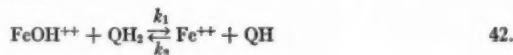
An attempt has been made to measure the rate of the $\text{Fe}^{++} - \text{H}_2\text{O}_2$ polarographically, by Kolthoff & Parry (150). There is a discrepancy of about 10^4 between their rate and Baxendale's, and they conclude somewhat pessimistically that "calculation of rate constants from kinetic currents does not yield reliable results." However, their method of calculation may be seriously in error. According to Kern (151), the kinetic current approaches with increasing time the value

$$i = n\mathcal{F}AC_0(Dk')^{1/2} \quad 41.$$

where i is the current, n the number of electrons transferred to the metallic ion (here one), \mathcal{F} Faraday's constant, A the electrode area, C_0 the bulk concentration of reducible ion (here Fe^{+++}), D its diffusion coefficient, and k' the pseudo-unimolecular rate constant. The Kern equation is based on the hypothesis that the Fe^{++} is diffusing away from the electrode, and reacting as it goes; while Kolthoff & Parry's computation is based on the assumption of an arbitrary finite reaction volume. If Kolthoff & Parry's data are substituted into Kern's equation, the rate constant calculated is in fairly good agreement with Baxendale's.

Glasner (152) has measured the rate of reaction of H_2O_2 with alkaline cupric citrate. Fordham & Williams (153) have allowed Fe^{++} to react with cumene hydroperoxide in the presence of acrylonitrile to trap the radicals formed; the second-order rate constant is $10^{10.9} e^{-12,000/RT} \text{ sec}^{-1} \text{ mole}^{-1} \text{ l}$. Davis, Evans & Higginson (154) have used the same technique to demonstrate that the reaction of Ti^{+++} with NH_2OH yields NH_2 radicals.

The reaction rates obtained by Baxendale, Hardy & Sutcliffe (155) for the reactions of ferrous and ferric ions with quinone and hydroquinone are consistent with the scheme

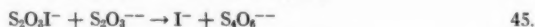
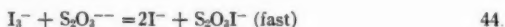


The authors have measured k_1 , k_4 , and the ratio k_3/k_2 .

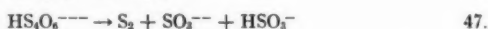
Kolthoff & Miller (156) have reported that the decomposition of $\text{S}_2\text{O}_8^{--}$ obeys a two-term rate law, indicating two independent paths. The first is uncatalyzed, has an activation energy of 33.5 kcal., and all the oxygen evolved by it originates in the solvent water. The second is acid-catalyzed,

has an activation energy of 26 kcal., the expected negative salt effect, and all the oxygen evolved by it originates in the peroxydisulfate. Fordham & Williams (157) find for the reaction of Fe^{++} with $\text{S}_2\text{O}_8^{--}$ the salt effect expected for a +2:-2 reaction, the second order rate constant being $10^{11} e^{-12,100/RT} \text{ sec.}^{-1} \text{ mole}^{-1} \text{ l.}$

Awtrey & Connick (158) find the rate law for the reaction of I_2 with $\text{S}_2\text{O}_3^{--}$ in agreement with that of Dodd & Griffith (159). The mechanism proposed is



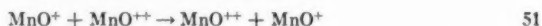
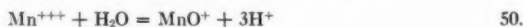
The authors have also studied the rate of the side reaction leading to SO_4^{--} , and (160) the reaction of I_2 with $\text{S}_4\text{O}_6^{--}$. The decomposition of thiosulfate in acid solution has been reinvestigated by Dinegar, Smellie & La Mer (161), and the sequence they propose is



Two authors have submitted kinetic evidence of the existence of soluble +4 manganese. Adamson (162) has shown that the rate of exchange of radio- Mn^{++} with MnO_4^- is given, within experimental error, by

$$\text{Rate} = k(\text{H}^+)^1(\text{Mn}^{++})^{3/2}(\text{MnO}_4^-)^{1/2}. \quad 48.$$

This rate law can be derived from the sequence



Merz, Stafford & Waters (163) have reduced permanganate with peroxide or ferrous, in the presence of isopropyl alcohol. As the ratio of alcohol to inorganic reducing agent increases, the number of equivalents of reducing agent consumed approaches three per mole of permanganate. The isopropyl alcohol is oxidized to acetone by the two-electron oxidizing agent, which the authors suggest is soluble Mn^{IV} .

Dusenbury & Powell (164) have reinvestigated the kinetics of the reaction of nitrous acid with ammonia, and also with methylamine, which they find to be second-order. The dependence of the rate upon pH suggests that the slow step is



Hofman-Berg & Holten (165) have found the second-order rate constant for the reaction of CS_2 with N_3^- to be $10^{13.4} e^{-21,100/RT} \text{ sec.}^{-1} \text{ mole}^{-1} \text{ l.}$ On the basis of this datum, they compute a chain length of 18 for the CS_2 -induced

reaction between azide and iodine. Some results on the thiocyanate-induced reaction between azide and iodine have been reported by Senise (166).

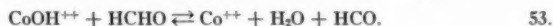
Mention has already been made of the evidence for hydrolyzed metal ions as the reactive species, in the cases of ferric and cupric with peroxide (149), ferric with hydroquinone and semiquinone (155), and manganese IV with manganese III (162). Like results are encountered in the reactions of ferric with neptunium IV (167), cerous with ceric (168), thalious with thallic (169), and iodine with titanous ion (170). Complexes with halide ions can also be reactive, viz., thalious with thallic (169), stannous with ferric (171), europous with europic (172), and stannous with stannic (173, 174).

Pinsent & Roughton (175) have made the most careful study yet of the reaction of CO_2 with water and with hydroxide ion. The first-order rate constant for the reaction with water, extrapolated to zero buffer concentration, is $(kT/h) e^{-4.6/R} e^{-17,200/RT} \text{ sec}^{-1}$. The second-order constant for the hydroxide reaction is approximately $(kT/h) e^{-12,000/RT} \text{ sec}^{-1} \text{ mole}^{-1} \text{ l}$.

Oxidation of organic compounds by inorganic oxidants.—The kinetics of oxidation of isopropyl alcohol by chromic acid has been investigated by Holloway, Cohen & Westheimer (176). In further support of the authors' hypothesis that the reaction proceeds through the formation of an intermediate chromate ester, they have isolated a stable solution of yellow di-isopropyl chromate. Duke & Bremer (177) have given kinetic evidence for the formation of ceric-glycol and ceric-di-glycol intermediates in the oxidation of 2,3-butanediol by ceric ion.

Rate data have been reported for the oxidation of aniline by sulfuric acid (178), uncatalyzed, and catalyzed by selenium, cupric, and mercuric ions. The reaction of oxalate with peroxydisulfate is strongly catalyzed by silver or cupric ions (179).

Bawn & White (180) have reported the kinetics of oxidation by Co^{+++} of water, formic acid, formaldehyde, and methyl, ethyl, and *n*-propyl alcohols. Where the effect of acidity has been determined, the reaction has been found slower at higher acidity; this suggests that the reactive species, at least in part, is CoOH^{++} or a more hydrolyzed ion. The oxidations of formic acid and of methanol proved to be first order with respect to each reactant. However, for formaldehyde and ethyl and *n*-propyl alcohol, the reaction order with respect to Co^{+++} drifted from first order at high Co^{+++} concentration to second order at low. This behavior suggests that the initial step is



Unfortunately, the effect of added Co^{++} was not investigated.

ORGANIC REACTIONS IN SOLUTION

Structure effects on reactivity: aromatic compounds.—One of the most valuable correlations of structure with reactivity is provided by Hammett's well known "sigma function" treatment, applicable to meta- and para-substituted aromatic compounds, which is expressed by

$$\log (k/k_0) = \rho\sigma$$

where k is a rate or equilibrium constant for the compound in question, k_0 the corresponding constant for the parent compound, ρ a parameter characteristic of the reaction, and σ a parameter characteristic of the substituent group. During 1951 the method has been applied to the ionization constants of catechols (181), the hydrolysis of tri-aryl-silanes (182), the hydrolysis of diphenyl ketimines (183), the acid strength and ester hydrolysis of the seven quinoline carboxylic acids (184), the acid strength and the reactivity with diphenyldiazomethane of *o*-toluic acids (185), the acidic and alkaline hydrolysis of benzamides (186), the fission into radicals of *tert*-butyl peroxybenzoates (187), the acetolysis of diazoacetophenones (188), the reaction of peroxybenzoate radicals with benzaldehydes (189), the reduction of iodo-phenols by HI (190), and the reaction of 2,4-dinitrofluorobenzene with anilines (191).

On the other hand, the pyrolysis of benzyl bromides (19) shows no correlation with the sigma-function; and the fission of substituted benzoyl peroxides in acetophenone (192) gives a curved line on the sigma-function plot.

Price & Lincoln (193) have suggested that the curiously large sigma value for the *tert*-butyl group arises from decreasing solvation stabilization. The same authors (194) have shown that dimethylamino groups hindered by adjacent methyl groups have smaller sigma values than unhindered dimethylamino groups; the effect is supposedly the result of steric inhibition of resonance between the dimethylamino groups and the ring. Swain & Langsdorf (195) have discussed Hammett's parameter ρ from the point of view of Swain's (196) "push-pull" theory of organic reactions. The irregularity of the sigma-function plot for the rate of alcoholysis of benzoyl chloride in 50 per cent aqueous acetone has led Brown & Hudson (197) to propose that in this solvent the solvolysis proceeds by two mechanisms, one unimolecular and the other bimolecular.

De la Mare & Vernon (198) have determined the partial reaction rates for each position in the ring, for the bromination of benzene and the mono- and di-methoxy substituted benzenes. For the bromination of benzeneboronic acid, the rate determining step is between Br_2 and $\text{C}_6\text{H}_5\text{BO}(\text{OH})^-$, according to Kuivila & Easterbrook (199). Berliner (200) has remeasured the kinetics of iodination of phenol, and concluded that the reaction mechanism involves phenolate ion and iodonium ion, I^+ . Derbyshire & Waters (201) have shown that the chlorination of $\text{C}_6\text{H}_5\text{—CH}_2\text{—SO}_3\text{Na}$ by hypochlorous acid is bimolecular, and the rate is proportional to the activity of hydrogen ion, so that Cl^+ may be the chlorinating species in a slow step. It may be mentioned that Bell & Gelles (202) have determined by an e.m.f. measurement the equilibrium constant for the formation of iodonium ion,

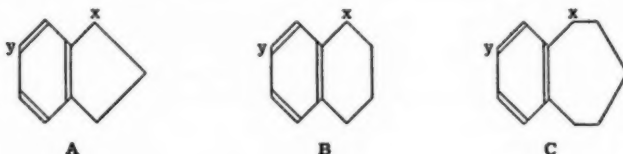


which they give as $K = 1.2 \times 10^{-11}$ at 25°C .

The subject of aromatic nucleophilic substitution has been reviewed by

Bunnett & Zahler (203). Bevan (204) finds the order of reactivity of *p*-nitro-halobenzenes toward ethoxide ion to be $\phi F > \phi Cl > \phi Br > \phi I$, which is just the reverse of the usual order. In explanation, he suggests that the *p*-nitro-halobenzenes possess an important resonance form in which the nitro group is negative and the halogen positive. The rates of exchange of radio- I^- with some aryl iodides have been investigated by Kristjanson & Winkler (205); the rates of exchange of radio- Br^- with some aryl and benzyl bromides, by Sugden & Willis (206).

Two groups of investigators have offered kinetic evidence of the steric hindrance of resonance in the activated state. Both have used derivatives of the ring compounds A, B, and C:



Baddeley & Chadwick (207) have studied the rates of solvolysis of the compounds which have a chlorine atom at point x, while Arnold & Truett (208) have studied the rates of solvolysis of the chlorides resulting from a C_6H_5-CHCl -substituent at point y. In both cases, the solvolysis rate is greatest for the five-membered ring compound and least for the seven-membered. The authors point out that the formation of the cationic activated complex is facilitated by a quinonoid resonance structure, which is most readily formed when the ring is planar.

Structure effects on reactivity: aliphatic compounds.—The role of steric repulsion in bimolecular reactions has been emphasized many times. A good example is provided by the amine catalysis of dealdolization, studied by Koob, Miller & Day (209); and the aminolysis of esters, studied by Arnett, Miller & Day (210). The reactivity of primary amines is much greater than that of secondary, and tertiary amines are quite ineffective. Moreover, the reactivity of the primary amines decreases in the order methyl, ethyl, isopropyl. This order of reactivity is so familiar for bimolecular reactions that McElvain & Tate (211), upon finding this structure effect in the reaction of chloride ion with iminoesters, can adduce it as evidence that the reaction is bimolecular.

The corresponding steric acceleration of unimolecular solvolyses has until recently escaped notice. Brown *et al.* (212) have reported the following solvolysis rates, in 80 per cent aqueous ethanol:

<i>tert</i> -butyl chloride	Rate = 1
methyl di-isopropyl carbinyl chloride	14
di-ethyl <i>tert</i> -butyl carbinyl chloride	48
tris- <i>tert</i> -butyl carbinyl chloride	600

Cardwell & Kilner (213) have published a kinetic study which bids fair to put new life into the old "alternating polarity" idea. They have determined the partial rates for the enolization of a number of ketones, by analyzing the bromination products and combining this information with the known kinetic data. They find that a methyl group adjacent to the potential double bond, at either end, increases the rate. An ethyl group gives a lower rate, a propyl group a higher, and *n*-butyl lower, an *n*-amyl higher, and an *n*-hexyl lower again. The alternation is very definite, and of considerable magnitude (about a factor of 1.5). The explanation offered by the authors is that because of hyperconjugation, the normal C—C bonds contain enough double-bond character so that a propyl or *n*-amyl group is effectively equivalent to a methyl group. This hypothesis seems to have been put forward first by Dewar (214).

It is increasingly the practice to determine the effect of substituents not only upon the reaction rates, but upon the heats of activation and the entropies of activation separately. Evans & Hamann (215) have given a theoretical discussion, based on their own kinetic data and others from the literature, of the systematics of entropies of activation for organic reactions. They point out, for unimolecular solvolyses, the trend of activation entropy with molal volume, with the halogen ionizing, and with the solvent composition; and, for bimolecular displacements, the trend with number and size of substituents, and with the nature of the incoming and outgoing halogen. The importance of the entropy of activation can also be noted in Tommila's data on the solvolysis of alkyl tosylates (216) and aryl sulfonyl chlorides (217). On the other hand, the first order hydrolysis of a series of bromo-acids is governed largely by the activation energies (218).

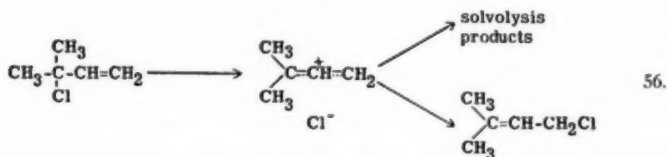
Several studies have been made of the reactivities of small-ring (cyclopropyl to cycloheptyl) compounds (219 to 223). The significant observation is the very small reactivity of cyclopropane and of cyclohexane as compared with the other ring compounds. Brown (221) ascribes the low reactivity to a high "I-strain," by which he means the change in internal strain which results from a change in co-ordination number of a ring atom involved in a chemical reaction.

Among other comparative kinetic studies published in 1951 are the following: the hydrolysis of the side-chain chloro and bromo derivatives of toluene (224); the acetolysis of *cis*- and *trans*-2-chloro- and bromo-cyclohexyl brosylate (225); the dehydrochlorination of benzene hexachloride isomers (226); the hydrolysis of a series of dipeptides (227); the esterification of 2- and 3-furoic acid and furanacetic acid (228); the alkaline hydrolysis of the two isomers of 3-chloro-6//7-cholestane-dicarboxylic acid (229); the oxidation of α - and β -D-glucose with HIO (230); the oxidation of *cis*- and *trans*-aminocyclanols with periodic acid and with lead tetraacetate (231); and the displacement reactions of *cis*- and *trans*-crotyl chlorides (232).

Rearrangements.—Lane & Walters (233) have measured the rate of the pinacol rearrangement for $C_6H_5CHBrC(OH)(C_6H_5)_2$, and find the rate con-

stant to be $(kT/h) e^{-4.6/R} e^{-25,400/RT}$ sec.⁻¹; they have measured also the rate of glycol formation and of epoxide formation. Aldridge & Murphy (234) find for the rate of conversion of ethyl-isopropenyl-allylmalonate into ethyl-1-methyl-4-pentenylidene-malonate $(kT/h) e^{-13.5/R} e^{-28,400/RT}$ sec.⁻¹, and from the large negative entropy of activation conclude that the reaction proceeds by way of a cyclic intermediate.

On the basis of a kinetic study of the acetolysis and simultaneous rearrangement of α,α -dimethylallyl chloride and γ,γ -dimethylallyl chloride, Young, Winstein & Goering (235) propose the following scheme:



Observation of the S_N2' reaction, a bimolecular anionotropic change, has been reported by Young, Webb & Goering (236) and by England & Hughes (237). The first investigators found the rearrangement in the bimolecular reaction of methylallyl chloride with diethylamine; the second, in the reaction of radio-Br⁻ with methylallyl bromide and crotyl bromide.

Witkop & Patrick (238) have investigated the rate of the rearrangement of 11-hydroxytetrahydrocarbazolenine into spiro-cyclopentane-1,2'- ψ -indoxyl. Carlin, Nelb & Odioso (239) have shown that the rearrangement of hydrazobenzene is second order with respect to H⁺, and that the benzidine/diphenylene ratio is independent of acidity or temperature. Calvin & Alter (240) have studied the *cis-trans* isomerization of four substituted stilbenes, and have concluded that *p*-nitro-*p'*-amino-stilbene isomerizes by a triplet path exclusively, while the other compounds isomerize by both triplet and adiabatic paths.

Bonner (241) has determined the rates in both directions for the anomerization of D-glucose pentaacetate. Nummy & Tarbell (242) give the rate of a Claisen rearrangement. Bordwell & Cooper (243) have measured the reaction rate of hydroxide ion with some α -chloro sulfones (the Ramberg-Bäcklund Reaction: HCl and SO₂ are split out, to yield the olefine).

Other mechanism studies.—Olson & Youle (244) have reported a study of the hydrolysis of β -butyrolactone. Bender (245), by following the rate of O¹⁸ exchange during ester hydrolysis, has demonstrated the presence of a stable intermediate, R—C(OH)₂(OR). The rate laws for the alkaline hydrolysis and the ethanolysis of β -diketones have been established by Pearson and co-workers (246). The hydrolysis of dimethylamides of phosphoric acids has been investigated by Heath & Casapieri (247).

Koefoed & Jensen (248) find that the hydrolysis of benzoyl and dibenzoyl phosphates includes an uncatalyzed, an acid-catalyzed, and a base-

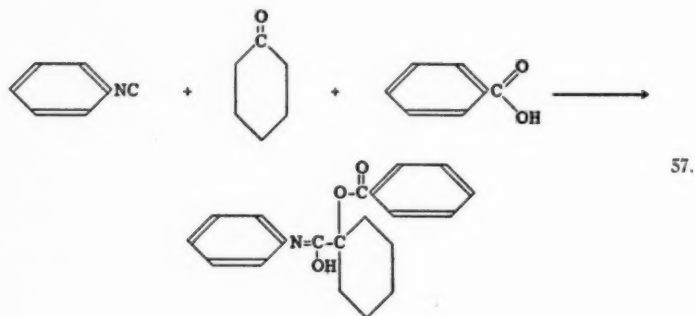
catalyzed path. The rate of reaction of acetyl phosphate with a number of amino acids has been determined at pH 7 and 39°C. by Koshland (249); the rates are so low as to exclude this nonenzymatic reaction as a step in peptide synthesis *in vivo*.

Bodforss & Ahrlund (250) report that the hydrolysis of trianisylmethyl perchlorate is both acid- and base-catalyzed. On the other hand, the reaction of vanillin with nitromethane is inhibited by either acid or base, and has a maximum rate in neutral solution, according to Crowell & Ramirez (251).

Brown (252) has reviewed the subject of thermal decarboxylation. Brown, Elliott & Hammick (253) have measured the rates of the uncatalyzed and the acid catalyzed decarboxylation of 2,4,6-trihydroxybenzoic acid; the rate of decarboxylation of the anion is negligible under their experimental conditions. Steinberger & Westheimer (254) have found in the decarboxylation of dimethylaloacetic acid a new class of ion-catalyzed reaction: not only do the mono-ion and the di-ion of the acid decarboxylate at comparable rates, but so also do the complexes of the acid with Cu^{++} , Al^{+++} , Ni^{++} , Mn^{++} , Fe^{++} , Fe^{+++} , and Pd^{++} .

The decomposition of ethyl xanthogenic acid has been found to be first-order with respect to the free acid (255). A number of reactions have been demonstrated to be kinetically second-order: the reaction of OH^- with DL-glyceraldehyde to yield fructose and sorbose (256); of thiourea with tetraacetyl- α -D-glucosyl bromide (257); of thiophenol with ethylenimines (258); of amines with ethylene oxide (259); of methylolithium and phenyllithium with butyl chlorides (260); of OH^- with N-nitroamines (261); and of H^+ with ethylnitrolic acid (262).

The Passerini reaction



is something of a kinetic curiosity, for it is third order; i.e., first order to each of its three organic reactants (263).

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THEORY OF IONIC CRYSTALS, SEMICONDUCTORS, AND DIELECTRICS¹

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THE SOLID STATE

During recent years there has been increasing activity in fundamental research on the solid state, particularly on ionic crystals, semiconductors, and dielectrics which have been found to have interesting and useful electrical and optical characteristics. The discovery of the useful properties of these substances has in part resulted from theoretical research on the solid state. The application of these properties to practical devices has stimulated further theoretical research on the solid state.

The electrical, optical, and structural properties of solids are determined, as are the chemical properties, by the outer shell or valence electrons which interact with the periodic lattice potential. The determination of the wave functions for electrons in the three-dimensional periodic potential of crystalline solids has been approached by two different approximations:

(a) The band theory was originally investigated by Bloch (1), Brillouin (2), and Wilson (3). It is essentially a molecular orbital method applied to the periodic lattice. The approximate one-electron wave functions involve the product of a periodic function and atomic wave functions $\psi_a(q - q_k)$:

$$\psi_K(q) = \sum e^{(i/\hbar)K \cdot r} \psi_a(q - q_k) \quad 1.$$

where $q - q_k$ is the vector displacement from the nucleus of the k atom and K is the wave number vector. In the cellular method of Wigner & Seitz (4) the atomic orbitals are modified to satisfy the boundary conditions of the unit cell before forming Bloch functions. Although these functions suffer from neither being exact solutions to the periodic lattice nor being orthogonal to each other, the collective electron model reveals qualitatively many properties of solids. The existence of broad bands of allowed energy levels, separated by broad bands of forbidden energy levels, was established by the band theory. So also was the sharp division of pure solids at low temperatures into metals and nonconductors, the former having partly filled or overlapping allowed bands, and the latter having all bands either completely filled or completely empty. Wannier (5) in treating excitation levels of insulators used modified atomic functions ψ_a' to obtain for the periodic lattice formal solutions which are exact and orthogonal. Slater (6) has recently suggested that it may be possible to apply these exact formal solutions to many theoretical problems of the solid state including perturbed periodic systems. The band theory has been most successful quantitatively with

¹ The survey of literature pertaining to this review was completed in December, 1951.

metals; however, it has also been useful qualitatively in interpreting the electronic properties of semiconductors and insulators.

(b) The Heitler-London method is, of course, the familiar atomic orbital method and is applicable to systems in which the electrons are localized on particular atoms. The approximate crystal wave functions are formed from antisymmetrical linear combinations of permutations of products of atomic wave functions:

$$\psi(q_1, q_2 \cdots q_N) = \frac{1}{N!^{1/2}} \sum_P^{N! \text{ terms}} (-1)^P P[\psi_a(q_1)\psi_b(q_2) \cdots \psi_n(q_N)] \quad 2.$$

for a system of N electrons. The terms are positive when the permutation P is even and are negative when P is odd. The atomic model adequately describes the properties of alkali halides, particularly when modified by including overlap effects and many-body interactions and using orthogonalized wave functions as has been done by Löwdin (7). The model has been recently used to describe impurities and defects in semiconductors. A limitation of the approach is that it does not naturally allow for electronic current. However, in the case of transition element oxides such as NiO, the electrical properties are in accord with the Heitler-London model, whereas the band theory does not appear applicable. From the atomic point of view a metal has unsaturated bonds, whereas ionic crystals possess saturated atomic orbitals, and homopolar insulators possess saturated covalent bonds. Pauling (8) has developed a resonating-valence-bond theory of metals and intermetallic compounds based on the existence of an extra or metallic orbital which permits uninhibited resonance of valence bonds thereby giving rise to metallic properties.

Recently Mott (9) has proposed that the band theory model and the Heitler-London model are not different approximations to the same exact wave function, but instead that the band theory is a good approximation for some systems, and the Heitler-London model is a good approximation for other systems. For crystalline solids with incomplete zones, such as metals or transition metal oxides, the collective electron model is applicable only if the interaction energies and interatomic distances are such that a high concentration of electron-hole pairs spontaneously form. In addition to the data on NiO and evidence by Coulson & Fischer (10) that the wave functions for H_2 undergo a similar change with increasing interatomic distance, Mott emphasizes that energy is always required to separate the electron and hole of the first pair formed, and only after approximately one pair per atom has been formed may mutual screening and increased binding energy reduce the total energy below that of the system with no electron-hole pairs. In metals this occurs; in transition element oxides, electron-hole pairs do not form spontaneously.

The self-consistent cellular method originated by Wigner & Seitz (4) for evaluating wave functions within a single cell of the crystal lattice has been refined by von der Lage & Bethe (11). The symmetry requirements of the

wave functions are satisfied by constructing suitable linear combinations of spherical harmonics, and the cell boundary conditions are satisfied at points more representative of the cell surface than have been used previously. The improved method has as yet been applied only to the Shockley empty lattice and to sodium metal.

In semiconductors and dielectrics, the electrical and optical properties are markedly dependent on impurities, lattice defects, and surface effects. It is to the quantitative treatment of the perturbed periodic lattice that much theoretical effort is being directed. Utilizing a theorem of Wannier, Slater (6) has elegantly simplified the problem of a perturbation that is slowly varying from one atom to the next. The modulation of the atomic wave functions is shown to depend only on the perturbing potential and on the eigenvalues for the unperturbed periodic lattice. The problem of electrons in perturbed periodic lattices is thereby reduced to the simpler problem of free electrons of an appropriate effective mass in the slowly varying perturbing potential. James (12) has obtained the solution for a slowly varying perturbation by joining together solutions valid for a single period of the unperturbed periodic potential.

IONIC CRYSTALS

Lattice energies of alkali halides.—The alkali halides are the simplest ionic crystals and have been investigated theoretically more thoroughly than has any other class of solids. The classical theory of ionic crystals was founded by Born (13) and Madelung (14) on the hypothesis that these substances consist of positively and negatively charged ions in an orderly array, held together by the coulomb interaction between the ions, and prevented from collapsing by the contact of the ions with each other. Since the coulomb bonds are nondirectional, the ions arrange themselves in a compact structure. The lattice sums connected with the coulomb attraction were first computed by Madelung. Born expressed the repulsion energy in the form b/r^n , and then evaluated the parameters b and n from the equilibrium interatomic distance and the compressibility, recognizing that at equilibrium the attractive coulomb force is equal to the repulsive force. The semi-empirical theory was further refined by Born & Mayer (15) by expressing the repulsion energy in an exponential form suggested by Pauling (16) from quantum mechanical considerations and by including a van der Waals attractive interaction. In addition to alkali halides, thallous and silver halides were treated. The lattice energy is:

$$E = -\frac{Ae^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + Be^{-r/\rho}. \quad 3.$$

The coefficients C and D of the dipole-dipole and dipole-quadrupole terms of the van der Waals interaction were obtained from dispersion data and suitable lattice sums. With this model Price (17) has computed the elastic constants (C_{11} — C_{12}) and C_{44} . Recently, effort has been made to calculate the

heat of formation and other properties of mixed crystals of alkali halides. Wallace (18), using the Born-Mayer model, was unable to obtain agreement with experiment; however, Durham & Hawkins (19), by recognizing that the ions are not at constant nearest-neighbor distance and by evaluating the positions of minimum potential energy, were able to compute successfully the average lattice constant, the heat of mixing, and the activity ratio in the solid solution.

Concurrently, strictly quantum mechanical methods have been applied to ionic crystals. By the one-electron approximation, Hylleraas (20) and Landshoff (21) have evaluated the cohesive energy of LiH and NaCl, respectively. Both utilize linear combinations of free ion wave functions that are not orthogonalized. Landshoff also calculated the compressibility of NaCl. Löwdin (7) has recently refined and extended the quantum mechanical investigation of alkali halides. The one electron approximation is assumed. Linear combinations of free ion wave functions neglecting mutual deformation of the ions are used. The radial part of the free ion wave functions are taken from self-consistent field calculations (22) including exchange. Linear combinations of the free ion wave functions are formulated so as to form a normalized and exactly orthogonalized set of functions:

$$\phi_\mu = \sum^N A_{n\mu} \psi_{n\mu} \quad 4.$$

and

$$\int \phi_\mu^* \phi_\nu d\tau = \delta_{\mu\nu} \quad 5.$$

for a crystal of N electrons, μ and ν refer to the atoms, and the coefficients $A_{n\mu}$ form a matrix. To include the effect of the overlapping of neighboring ions, Löwdin introduces overlap integrals:

$$S_{\mu\nu} = \int \psi_\mu^* \psi_\nu d\tau - \delta_{\mu\nu} \quad 6.$$

which are other than zero only for a pair ψ_μ and ψ_ν associated with different ions and the same spin. The cohesive energy is then derived and found to contain a term having the characteristics of a many-body interaction. The existence of a many-body interaction explains the failure of the alkali halides to satisfy the Cauchy relation $C_{12} = C_{44}$ for cubic crystals of ions interacting only with central forces. In addition to computing the cohesive energy, Löwdin successfully evaluated the lattice constant, the compressibility, and the elastic constants of several alkali halides, including LiCl, NaCl, and KCl. Benson & Wyllie (23) have attempted a greatly simplified quantum mechanical treatment for LiF assuming the cation to be a point positive charge, and have been forced to adjust their wave functions to fit diamagnetic data in order to obtain reasonable cohesive energy and equilibrium interatomic distance. In the derivation by Szigeti (24) of the relation between compressibility and absorption frequency of ionic crystals, the deformation of the

spherically symmetrical electronic configuration of each ion has been described by a dipolar term and a local distortion arising from the repulsive forces. Radkowsky (25) has shown that lattice vibrations broaden the energy levels of polar crystals, thereby creating a change in the valence-conduction band gap with temperature.

Solid-state luminescence.—The alkali halide phosphors have been extensively investigated to determine the mechanism of solid-state luminescence. Seitz (26), utilizing the extensive data of Pohl and associates, qualitatively showed that the properties of thallium-activated alkali halides were related to energy levels of the free thallous ion and emphasized the importance of the Franck-Condon principle and atomic rearrangements in determining absorption and emission spectra. Williams (27) has recently reported a quantitative calculation of the absorption and emission spectra of thallium-activated potassium chloride. The radial charge densities of the free thallous ion in the ground 1S_0 and excited $^3P_1^0$ states were calculated by the Hartree self-consistent field method and used to evaluate the polarizabilities, ionic radii, and compressibilities of these ions interacting with the chloride ion. The 1S_0 and $^3P_1^0$ Tl^+ were then substituted in dilute concentration for K^+ in KCl, and the potential energy as a function of atomic configuration was computed. In addition to the usual Madelung, van der Waals, and repulsion energy of the Born-Mayer theory, ion-induced dipole interactions resulting from asymmetry in ion positions were included as well as electrostatic overlap corrections for the excited state. It was shown that only the interactions of the Tl^+ with the nearest Cl^- neighbors are markedly dependent on the state of the activator; therefore, the system for each electronic state of the Tl^+ is adequately described by the dependence of the energy on the Tl^+ nearest Cl^- distance, with the additional condition that the remainder of the lattice rearranges to minimize the potential energy. The absorption spectrum is then computed by weighting each transition energy by a Boltzmann factor for the probability of the configuration of the ground state that yields that transition energy, and a Jacobian factor for the change of variable from configuration to transition energy. Similarly, the emission spectrum is computed by summing over configurations characteristic of the excited state. At low temperatures the effect of the quantum mechanical zero point energy must be included. Williams & Hebb (28) have refined the final spectral calculation by evaluating the matrix elements for transitions from individual vibrational levels of the initial state to individual vibrational levels of the final state. In general, the luminescence of alkali halide phosphors is characterized by highly localized activator wave functions for both the ground and emitting states and by localized atomic rearrangements accompanying luminescence.

Johnson & Williams (29) have formulated a general theory of the dependence of luminescent efficiency on activator concentration, based on the idea that activator ions are capable of efficient emission only if isolated from other activator ions. The presence of nearby activator ions reduces the activation

energy for radiationless de-excitation, probably by overlap of wave functions; therefore, the efficiency-concentration interrelation is markedly temperature dependent.

Förster (30) has proposed a dipole-dipole interaction mechanism to explain the efficient transfer of excitation energy from sensitizing impurities to luminescent impurities. So far the mechanism has been applied only to organic phosphors where energy transfer between molecules 70 Å apart has been computed. The mechanism probably operates in inorganic systems, also.

Lattice defects and electron traps.—Frenkel (31) first suggested that a crystal in thermodynamic equilibrium contains imperfections and proposed that ions may leave lattice sites and occupy interstitial positions. Schottky (32) subsequently proposed that an energetically more favorable type of imperfection, particularly for compact lattices such as alkali halide crystals, involves removing a positive and a negative ion from their lattice points and placing them on the surface of the crystal. The ionic conductivity, diffusion, and many optical and electronic properties of alkali halides are dependent on Schottky imperfections. Mott & Littleton (33) have calculated the energy required to remove an ion from the perfect lattice and the activation energy required to transport a neighboring ion into the vacancy. The Born model was used with a special modification to evaluate the polarization around the point charge in the lattice with the ions fixed. The polarization calculation is complicated by the dipole induced on any one ion arising from the dipoles at all other lattice points as well as from the charge on the vacancy. Mott & Littleton, in the zero order approximation, assume a continuum to evaluate the dipole moment on each ion but treat the total polarization as constituted of an array of induced dipoles at lattice sites. In the first order approximation, the remainder of the lattice is regarded as a continuum in calculating dipoles, and the field at each of the six nearest neighbor sites is evaluated by summing over all other sites. Higher orders to the fourth were so evaluated and the results found to converge. Rittner, Hutner & du Pré (34) have refined these calculations to the eighth order and have also determined the polarization energy around two adjacent charges in the rigid lattice. For the single charge, tabulated results are given by these authors for many oxides, sulfides, and tellurides, as well as for the silver and alkali halides. Dienes (35) has evaluated the activation energy for the diffusion of coupled pairs of vacancies using a Born-Mayer model and including the effect of nearest-neighbor distortions of the lattice. A theoretical activation energy of 0.375 eV for KCl suggests that migration of neutral pairs of vacancies may dominate diffusion phenomena.

Experimentally, F centers in alkali halide crystals have been exhaustively investigated by Pohl and associates. It was first suggested by de Boer (36) that an electron trapped at an anion vacancy was responsible for the color center. Gurney & Mott (37) have emphasized that at large distance r from the vacancy the trapped electron experiences an electrostatic field e/Kr^2 where K is the dielectric constant, and therefore that a series of stationary

states leading up to a series limit exists. The lowest state is a $1s$ state, and the absorption band of the F-center corresponds to a transition to the $2p$ state. Seitz (38) has reviewed diverse data on color centers verifying the identification of the F-center. For NaCl, Tibbs (39) calculated the $1s-2p$ transition energy as 1.3 eV and the oscillator strength as 0.6 by using wave functions numerically computed for a coulomb potential sawed off at small r . A transition energy of 2.2 eV, which is in agreement with the experimental 2.7 eV, was obtained by Simpson (40), who used the coulomb potential at large r , and at small r a square potential well with dimensions determined by the charge and induced dipoles of the surrounding ions. The component of the field arising from the low frequency polarization of the medium by the wave function of the electron was included by a self-consistent treatment. The variation method was used with one parameter wave functions. Similarly Simpson determined radial charge densities and energy levels of electrons trapped at negative ion vacancies in AgBr and at interstitial positive ions in NaCl and AgBr. Electrons trapped at negative ion vacancies are found to have more localized wave functions and greater binding energies than electrons trapped at interstitial positive ions.

The width of the F absorption band arises from coupling of the center with lattice vibrations. Huang & Rhys (41) have formulated a theory based on the Franck-Condon principle to explain quantitatively the shapes of F-bands. They assume a dielectric continuum and in determining vibrational wave functions consider the F-center as a static charge distribution. In fitting the theory to experiment, several parameters are determined arbitrarily. In addition, Huang & Rhys have attempted to evaluate the probability of nonradiative de-excitation of an F-center.

Self-trapping of electrons in polar crystals was predicted by Landau (42). The binding energy is presumably produced by ionic displacements induced by the field of the trapped electron. Markham & Seitz (43) have calculated the binding energy of an electron trapped near the cation in NaCl. A sawed-off coulomb field with the depth determined by the method of Mott & Littleton (33) was used. A self-consistent solution was obtained by requiring that the wave function used to determine the potential well be the same as the wave function obtained from the potential well on solving the Schrödinger equation. The radial charge density is found to be quite extensive, and the thermal binding energy is only 0.13 eV, so that self-trapping is expected only at very low temperatures. Fröhlich, Pelzer & Zienau (44) have also considered the problem of self-trapping. They assume a continuous dielectric medium with a single vibrational frequency and find that the energy of interaction depends very little on the average velocity of the electron. Therefore, the existence of self-trapping appears doubtful.

SEMICONDUCTORS

Semiconductors are a broad class of elemental and compound substances exhibiting electronic conductance intermediate between the conductance of metals and insulators. In contrast to metals their electronic conductance

increases with increasing temperature, at least at low temperatures, indicating that the number of current carriers is increasing with temperature. From the point of view of the band theory, semiconductors are considered to have a filled valence band and an empty conduction band at absolute zero of temperature. The electrons in the valence band are, of course, mobile; however, no net charge can be transported in an applied field because all states within the valence band are occupied, and the Pauli principle forbids putting two electrons in the same state. In the case of intrinsic semiconductors, the forbidden band gap is sufficiently small so that at ordinary temperatures electrons may be thermally excited from the valence to the conduction band, and charge transport is now feasible in both bands. Impurity or defect semiconductors are characterized by nonperiodicity in the lattice, yielding discrete localized states in the forbidden band gap. If these states are normally occupied, the system can be thermally excited to yield conduction electrons; if they are normally unoccupied, the system can be thermally excited to yield empty states in the valence band. The former yield N-type; the latter, P-type semiconductors.

Band structure.—The quantitative calculation of the widths of the allowed and forbidden bands of semiconductors has experienced limited success. Following the procedure that Kimball (45) used on diamond, Mullaney (46) has performed for silicon a Wigner-Seitz computation of electronic energy bands. The Wigner-Seitz polyhedron is sixteen-sided having four large hexagonal faces at the centers of which the boundary conditions of continuity of the wave functions, their normal and tangential derivatives are applied. Two polyhedra are simultaneously considered because of the two atoms in the unit cell. A linear combination of fourteen s , p and d wave functions yielded a valence band width of 16 ev and a forbidden band width of 11 ev, compared to experimental values of 19 ev and 1.1 ev, respectively. Omitting the d orbitals results in even poorer agreement. The disagreement of theory and experiment for the band gap can be attributed to the Wigner-Seitz method being fairly good for the ground state but leading to erroneous results for excited states.

The electronic energy bands of graphite have been computed by Wallace (47). Bloch wave functions consisting of linear combinations of products of periodic functions and $2p_z$ atomic orbitals were used in the "tight binding approximation" by a variational scheme. The zone structure was evaluated for a single hexagonal layer and for the three dimensional lattice. The theoretical zone structure indicates that graphite is a semiconductor with the lowest filled Brillouin zone in contact at twelve points with the next Brillouin zone; therefore, the band gap is zero. A marked temperature dependence of the anisotropy of electronic conductance and a large anisotropic diamagnetic susceptibility for the conduction electrons are predicted, and the optical absorption spectrum of graphite is explained.

The origin of the temperature dependence of the forbidden band width in nonpolar semiconductors such as germanium and silicon has been con-

sidered by several investigators. Möglich, Riehl & Rompe (48) recognized the effect of lattice vibrations in broadening the energy levels and thereby reducing the band gap with increasing temperature. Radkowsky (25) demonstrated theoretically that this effect is large for polar crystals but negligible for nonpolar crystals. Bardeen & Shockley (49) have treated the effect of lattice expansion on the energy gap and have concluded that thermal expansion cannot account for the observed shift with temperature of the absorption edge in germanium and silicon. Fan (50) has considered the effect of lattice vibrations in shifting the energy levels, rather than broadening them. The calculation is based on the idea that a crystal with a vibrating lattice will have a different electron-lattice interaction energy than a rigid lattice, and the difference in energy of the excited and ground state will not be the same for a vibrating and a rigid lattice because of the difference in electron-lattice interaction for the two states. By computing the band gap in a vibrating crystal, Fan obtains a contribution to the temperature dependence of the band gap which, added to the contribution from thermal expansion, gives good agreement with the experimental shift of absorption edge for silicon but poor agreement for germanium.

Germanium and silicon have been investigated as intrinsic and as N and P-type semiconductors. Both substances have the diamond structure with each atom making sp^3 tetrahedral covalent bonds with the four nearest neighbors. Thermal excitation of an intrinsic semiconductor to produce an electron in the conduction band and a positive hole in the valence band corresponds, as emphasized by Shockley (51), to removing an electron from a covalent bond. Statistical theory (52) reveals that independent of whether the semiconductor is intrinsic, N, or P-type, the product of the concentration of electrons in the conduction band n_e and the concentration of positive holes in the valence band n_h is:

$$n_e n_h = 4(2\pi m k T / h^2)^3 (m_e m_h / m^3)^{3/2} e^{-E_G / k T} \quad 7.$$

where m is the free electron mass, m_e and m_h are the effective masses of the conduction electron and positive hole, and E_G is the band gap. Clearly the number of carriers increases rapidly with temperature for $kT < E_G$. For an intrinsic semiconductor, n_e will equal n_h at any temperature and will vary with temperature predominantly by the factor $e^{-E_G / 2kT}$.

Impurity semiconductors.—In germanium and silicon suitable impurities can substitute in dilute concentrations at lattice sites and dominate the electronic properties. Torrey & Whitmer (53) suggested that a Group V impurity atom with one more valence electron than is necessary to make four covalent bonds may substitute in germanium or silicon. Pearson & Bardeen (54) reported that phosphorus dissolves substitutionally in silicon. The extra electron in its state of lowest energy will be bound by the extra positive charge of the impurity atom, but may be thermally excited to the conduction band. This is an N-type semiconductor and the impurity is considered a donor. Similarly an impurity atom from the third group of the periodic

chart such as boron requires an extra electron to form the four covalent bonds with the neighboring silicon atom. Formation of these bonds, therefore, yields a positive hole which in its state of lowest energy will be bound by the extra negative charge of the impurity atom, but may be thermally excited to the valence band. This is a P-type semiconductor, and the impurity is considered an acceptor.

The electron of the donor and the positive hole of the acceptor move in hydrogen-like orbits about their respective ions. Bethe (55) showed that since the radius of the orbit is large compared to the radius of the ion, only the coulomb field of the ion, which has been reduced by the dielectric constant K of the medium, determines the binding energy. The ionization energy is given by the Bohr formula:

$$E_I = 2\pi m^* e^2 / K^2 h^2. \quad 8.$$

Substituting the free electron mass for the effective mass m^* , E_I equals 0.05 ev for germanium and 0.08 ev for silicon in fair agreement with experimental ionization energies for semiconductors containing low concentrations of donors or acceptors.

Pearson & Bardeen (54) have observed a decrease in ionization energy of carriers in silicon with increasing concentration of donors or acceptors and have suggested that the coulomb interaction of carriers and ionized impurities is responsible. However, the experimental evidence suggests that the ionization energy depends on the total impurity concentration rather than on the ionized impurity concentration. Castellan & Seitz (56) have been unable to reconcile theory and experiment by considering the overlapping of carriers on different impurity ions, the polarization of neutral impurity atoms by carriers and ions, and statistical fluctuations in concentration of impurity atoms.

If both donors and acceptors are present in a semiconductor, the impurity present in the greater concentration will determine whether the semiconductor is N or P-type. For an N-type semiconductor containing N_D concentration of donors and N_A concentration of acceptors, the law of mass action can be applied, because of the dilute character of the system, to yield the concentration of conduction electrons n_e :

$$n_e(n_e + N_A)/(N_D - N_A - n_e) = \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{-E_D/kT} \quad 9.$$

where E_D is the ionization energy of the donors. The corresponding expression for a P-type semiconductor is obvious. These equations can also be derived more generally from Fermi statistics according to which the occupational probability of a state of energy ϵ is:

$$f(\epsilon) = \frac{1}{1 + e^{(\epsilon - \zeta)/kT}} \quad 10.$$

where ζ , the Fermi energy or chemical potential for electrons, is the energy for $f(\epsilon)$ equal to $\frac{1}{2}$ and is evaluated by integrating the product of $f(\epsilon)$ and

$n(\epsilon)$, the density of states, over the energy so as to equal the total number of electrons.

Electrical conductance is determined not only by the concentration of current carriers, but also by their mobility or drift velocity with unit applied field. Mobility in general is limited by deviations from the perfect periodic potential. At high temperatures or with low impurity concentration, the mobility of electrons or holes in semiconductors is determined by scattering by lattice vibrations. Wilson (57) and Seitz (58) have treated theoretically the scattering of electrons by acoustical vibrational modes and have concluded that the scattering is elastic and isotropic and that the mean free path is independent of electron velocity and is inversely proportional to the absolute temperature. The mobility then varies as $T^{-3/2}$, as is observed in pure samples of germanium, silicon, and tellurium. Bardeen & Shockley (59) have recently re-analyzed the interaction between electrons and the acoustical modes of vibration and have shown that the very high mobilities of electrons and holes in germanium are related to the small change in energy gap with dilation of the lattice. At low temperatures or with high impurity concentration, the mobility is limited by impurity scattering. Conwell & Weisskopf (60) have computed the scattering of conduction electrons by impurity ions and have shown that the mobility so limited is proportional to $T^{+3/2}$.

Barriers in semiconductors.—When a metal and a semiconductor are brought into contact with no applied electrical field, charge is transported until the Fermi energy is an invariant of the system. The transferred electrons, or holes, and the ionized donors, or acceptors, form a double layer which just compensates for the original difference in work function of the two substances. According to the Mott-Schottky theory (61) of rectification the potential ϕ of the barrier of width λ is:

$$\phi = (2\pi N e \lambda^2) / K \quad 11.$$

where N is the concentration of donors or acceptors in the semiconductor, and the current i through the contact is:

$$i = A \lambda e^{-e\phi/kT} [e^{eV/kT} - 1] \quad 12.$$

where V is the applied potential. The asymmetry of the barrier permits easy flow of electrons from an N-type semiconductor or holes from a P-type semiconductor to the metal, whereas the reverse process in each case occurs with difficulty. The Mott-Schottky theory adequately explained many properties of rectifying contacts; however, it predicts a marked dependence of rectification on the work function of the metal, an effect not observed with germanium and silicon semiconductors.

Utilizing an early suggestion of Tamm (62) on the existence of states in the forbidden band gap and localized on surfaces, Bardeen (63) proposed that the presence of surface states on semiconductors produces a barrier which is unaffected by contact with a metal. Equilibrium is established be-

tween electrons or holes in surface states and donors or acceptors in the interior of the semiconductor. Assuming that the surface charge ($N_s e$) must equal the ionized donors or acceptors in the barrier ($N_e \lambda$), ϕ takes the form:

$$\phi = 2\pi e N_s^2 / NK. \quad 13.$$

When contact is made with a metal, the difference in work functions of the metal and semiconductor is compensated by the surface state charge. Markham & Miller (64) have shown that the surface state model yields, as observed experimentally, a negligible temperature dependence of the work function of semiconductors. The existence of additional energy levels at the surfaces of germanium or silicon is not surprising considering that unpaired orbitals must occur at clean surfaces of these substances and gases are certainly readily chemisorbed. Aigrain, Dugas & Etzel (65) have, in fact, proposed a model for N-type germanium consisting of a P-type surface layer with monotonically decreasing concentration of acceptors and increasing concentration of donors from the surface into the bulk germanium. They are able to compute many electrical characteristics from the model and suggest that the acceptors arise from the diffusion of oxygen from the surface into the lattice during polishing or forming. The surface states on germanium and silicon, therefore, probably have their origin in impurities at the surface, rather than in the mere existence of the surface.

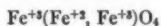
An N-type semiconductor in contact with a P-type semiconductor forms a rectifying junction. With no applied field the Fermi energy is again invariant. With an applied electric field in the direction to urge holes from the P-type region to the N-type region and electrons from the N-type region to the P-type region current flows easily, whereas with opposite polarity electrons and holes are exhausted from the contact, a space charge develops, and negligible current flows. P-N rectifying junctions of germanium have been studied theoretically by Shockley (66). Recombination of the injected holes with electrons and injected electrons with holes in the N and P regions, respectively, occurs. Lehovec, Accardo & Jamgochian (67) have shown that the recombination of holes and electrons injected through P-N boundaries in silicon carbide crystals may occur with emission of light.

The ability of semiconductors to conduct by holes in the valence band and electrons in the conduction band, plus the very high mobility of these carriers in germanium, permits holes injected into N-type germanium from one electrode to influence the current through another electrode operating in a different circuit. Crystal triodes or transistors operating on this principle were discovered by Bardeen & Brattain (68) and have been investigated theoretically by Shockley (66, 69).

Transition metal oxides.—The properties of the transition metal oxide semiconductors have been qualitatively interpreted with rather striking conclusions. For example, NiO crystallizes in the rock salt structure and clearly on the basis of the band theory should contain an unfilled zone because of the incompletely filled 3d shell of Ni^{+2} . However, the electronic

conductivity is low. Mott (9, 70) and de Boer & Verwey (71) have emphasized that the collective electron model is not applicable to these substances because of insufficient overlapping of the unfilled $3d$ orbitals of neighboring Ni^{+2} . Therefore, the formation of lattice wave functions from atomic wave function by the Heitler-London method is appropriate. The electronic conductivity can be considered as arising from converting one Ni^{+2} to Ni^{+3} and another Ni^{+2} to Ni^{+1} . The difference between the third and the second ionization energy of nickel minus the polarization energy resulting from the extra positive and negative charge in the lattice will be required for the excitation, and the conductivity is low.

Magnetic iron oxide, Fe_3O_4 , on the other hand, exhibits high electronic conductivity. Verwey & de Boer (72) have attributed this to the spinel-type crystal structure described by the formula:



which indicates that one of the two cation crystallographic sites accommodates either Fe^{+2} or Fe^{+3} in equal concentration. Above $120^\circ K.$, the Fe^{+2} and Fe^{+3} are distributed at random over these sites; therefore, the electrons can be easily transferred from Fe^{+2} to Fe^{+3} and the electronic conductivity is high. In general, the presence of ions of the same element with different valences distributed randomly at equivalent lattice sites yields high electronic conductivity.

Verwey (73) describes three types of oxide semiconductors: (a) Non-stoichiometric compounds containing anion or cation vacancies and an equivalent amount of anions or cations in different valence states; for example, FeO containing excess oxygen and equivalent Fe^{+3} . Wagner (74) has applied the mass action principle to substances of this type. (b) Diluted conductors such as Fe_3O_4 which have had some Fe^{+2} or Fe^{+3} at the variable valence site replaced by cations such as Mg^{+2} or Al^{+3} having invariant valency. With increasing substitution the activation energy for electronic conduction increases. (c) Controlled valency semiconductors contain impurities which facilitate the presence of ions of the same element with different valences at equivalent lattice sites; for example, Li_2O added to NiO yields;



which exhibits increasing conductance and decreasing activation energy for conduction with increasing δ . The principle of controlled valency, according to Kröger (75), operates in zinc sulfide phosphors where he maintains that added chloride ions facilitate the silver or copper activators in the monovalent state to substitute at divalent zinc lattice sites.

DIELECTRICS

Dielectric breakdown.—Insulators cease to exhibit negligible conductance at rather critical, high electric fields and instead catastrophically increase in conductance. Ionic conductance or thermal instability is often present

experimentally; however, ultimate dielectric strength in simple pure substances such as alkali halides or diamonds has been shown to be limited by strictly electronic effects. Intrinsic dielectric breakdown has been extensively investigated theoretically.

Zener (76) proposed that breakdown occurs when the electrostatic field becomes great enough for transitions to take place from the valence band to the conduction band by a process related to the quantum mechanical tunnel effect. Houston (77) and Franz (78) calculated the probability of field ionization, and calculated breakdown fields at least an order of magnitude greater than those found experimentally. In addition, the model fails to explain the decrease in dielectric strength with decreasing temperature observed below room temperature with alkali halides. The breakdown field for the Zener mechanism has a parabolic dependence on forbidden band width; therefore, dielectric strength would seem most likely to be limited by this mechanism for substances with small band gaps. Shockley (79) has recently demonstrated Zener breakdown in P-N junctions of germanium.

Von Hippel (80) originally proposed an electron avalanche theory on which much recent theoretical work on breakdown is based. He conceived that a conduction electron in an electrostatic field will be accelerated by the field and retarded by interaction with the vibrational modes of the lattice and postulated that breakdown occurs when the average electron gains energy from the field more rapidly than it loses energy to the lattice for all velocities less than the velocity required to produce ionization by impact. He also assumed that the concentration of conduction electrons is low enough so that collisions with the lattice vibrations are more probable than collisions with other conduction electrons. This is the case for crystalline dielectrics at moderate temperatures. Von Hippel emphasized that for polar substances the energy loss to the lattice is most probable when the conduction electron has kinetic energy equal to the energy of the optically active mode of lattice vibration, and therefore, that the breakdown field is the field required to accelerate the electron through this critical thermal range of velocities. Seeger & Teller (81) made a classical calculation of breakdown fields according to this mechanism. Although the quantum mechanical perturbation method is not strictly applicable to the energy loss calculation because of the short mean time between collisions, Callen (82) recently used a perturbation technique originated by Fröhlich (83) to calculate dielectric strength according to the von Hippel criterion of breakdown. Including the effect of the random motion of the electron and taking account of the electronic polarizability of the ions, Callen obtained theoretical breakdown fields for alkali halides in good agreement with experiment. He also concluded that, although the breakdown field is determined by slow electrons, breakdown paths are determined by fast electrons.

An impact ionization theory modified by a less stringent requirement for breakdown has been proposed by Fröhlich (83, 84, 85). He requires that the field be sufficient to exceed the losses to the lattice for conduction electrons

capable of ionizing valence electrons. In other words, breakdown is determined by the properties of high energy electrons on the tail of the distribution near ionization energies.

Independent of whether the low or high energy criterion for breakdown is used, the avalanche theory yields for crystalline polar insulators at low or moderate temperatures, approximately correct breakdown fields, and an increase in breakdown field with temperature and impurity content as observed. Meyer & Herman (86) have calculated by the method of Seeger & Teller the increase in dielectric strength of alkali halides arising from trapping by ionized F-centers. Seitz (85, 87) has proposed that the nonpolar coupling between conduction electrons and lattice vibrations is comparable with polar coupling and is maximal at high energies. The differences between the von Hippel and the Fröhlich theories of breakdown in polar substances are therefore less significant. In nonpolar substances with near-breakdown fields average electron energies are found to be surprisingly high, and an appreciable fraction of the electrons attain sufficient energy to excite impurity atoms. Seitz shows that statistical fluctuations in which conduction electrons suffer unusually few collisions with the lattice initiate breakdown. Avalanches of 10^{12} electrons ionized by impact accompany breakdown. Heller (88) has recently applied the steady-state Boltzmann kinetic equation to electrons in a nonpolar insulating crystal with an external field and has obtained a suitable distribution function revealing that the ionizing fluctuations governing breakdown are present in the steady-state solution.

In crystalline dielectrics at high temperatures or in amorphous dielectrics at moderate temperatures, the concentration of electrons in the conduction band may be great enough for collisions among conduction electrons to be more frequent than collisions between conduction electrons and lattice vibrations. In this case, the preceding theories that trace the series of events that an individual electron experiences are not applicable. Instead, as Fröhlich (89) and associates have emphasized, the conduction electrons in strong fields are characterized by an electronic temperature greater than the lattice temperature. Breakdown occurs at the field which yields an electronic temperature great enough for the rate of transfer of energy from the field to the conduction electrons to be greater than the rate of energy transfer to the lattice vibrations. Their model involves equilibrium between conduction electrons and trapped electrons, as well as among the conduction electrons. The critical field is computed to be:

$$F^* = Ce^{\Delta V/2kT} \quad 14.$$

where C is a constant, T is the lattice temperature, and ΔV is the depth of shallow traps. The breakdown strength of crystalline dielectrics at high temperatures and of amorphous dielectrics at moderate temperature therefore decreases with increasing temperature as observed experimentally, and the theoretical time constants involved appear to be in accord with experiment.

Ferroelectrics.—Much theoretical activity has been recently directed at explaining the ferroelectric properties of barium titanate. Above the Curie temperature of 118°C. the crystal is cubic with a barium ion at each corner, an oxygen ion in the center of each face, and a titanium ion at the center of the cube. Between 118°C. and 5°C. the substance is tetragonal and permanently polarized. The axis in the direction of polarization is expanded, and the axes perpendicular to polarization are contracted. Below 5°C., other transitions altering the symmetry and direction of polarization occur. Barium titanate possesses a strikingly high dielectric constant, and in the spontaneously polarized state exhibits hysteresis in polarization versus applied field.

Ginsburg (90) initiated a thermodynamic treatment of barium titanate according to a method earlier applied to Rochelle salt by Mueller (91). Devonshire (92) has successfully extended the phenomenological theory. He expanded the free energy in powers of the polarization and strains; evaluated the coefficients from the transition temperatures, the dielectric constant of the cubic form, and the strain and saturation polarization at one temperature for the tetragonal form; and finally, predicted the dielectric constants of the permanently polarized forms and the strain and saturation polarization of the orthorhombic and rhombohedral forms. The analysis strongly suggests that the structure change at 118°C. is a first order transition. Kittel (93) has used similar methods to investigate the antiferroelectric state.

The high dielectric constant and the spontaneous polarization of barium titanate arise from the catastrophic Clausius-Mosotti relationship between the dielectric constant K and the polarizabilities α of the constituent ions:

$$\frac{K-1}{K+2} = \frac{4\pi}{3} N \sum_i \alpha_i. \quad 15.$$

In general, the summation may include structural and local field corrections, as well as a polarizability for each ion. The dielectric constant becomes infinite as the above expression, with only moderately large polarizabilities, approaches unity. The compact perovskite structure has a high density of polarizable ions. Megaw (94) first pointed out that if the barium titanate lattice is constructed of rigid spheres with the usual ionic radii, the titanium ion is not in contact with its neighbors and therefore should exhibit a large ionic polarizability. In addition, Jonkers & van Santen (95) emphasize that a correction favoring the catastrophe should be applied to the Clausius-Mosotti equation to take account of the lack of cubic symmetry around the oxygen ions in barium titanate. Mason & Matthias (96) have developed a theory based on the titanium ion having six equilibrium positions because of covalent bonding with oxygen ions. Above the Curie temperature, the choice of positions would be random; below the Curie temperature, ions would be ordered within a domain. They require an unreasonably low local field at the titanium site to fit their theory to experiment. Devonshire (92)

has deduced from a Born model that the most stable position of the titanium is at the center of the cube. Roberts (97) has examined the dielectric properties of a large number of compounds and concluded that the total dielectric polarizability of an ion, like the electronic component, is independent of environment and therefore additive. The dielectric polarizability is interpreted as determined by the approximately invariant conditions of restraint of the neighboring ions, as well as by the electronic structure of the ion. Substitution of the dielectric polarizabilities into the Clausius-Mosotti equation yields satisfactory dielectric constants, even for barium titanate where the treatment is not rigorously applicable. Slater (98) has calculated, taking into account the precise crystal structure, the local fields at the titanium and oxygen sites. These fields are found to be much larger than the Lorentz field involved in the derivation of the Clausius-Mosotti equation, and Slater concludes that even a relatively small ionic polarizability for the titanium ions will yield ferroelectricity. The temperature dependence of the dielectric properties of barium titanate has not as yet been quantitatively explained by the atomic model.

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EXPERIMENTAL CRYSTALLOGRAPHY¹

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This chapter does not pretend to give complete coverage of all important crystal structure papers which appeared in the open literature in 1951. It is also inevitable that the particular interests of the reviewer are reflected in the space allotted to the various subdivisions of the chapter. Many crystal structure results for organic salts where the determination of the molecular structure was the main purpose of the investigation have been left entirely out of consideration, since they are covered in the chapter, "Experimental Molecular Structure," to which the reader is referred.

Preliminary reports of structural work have not been taken into account unless there is evidence that the investigation has reached such a state of completion that final conclusions as to the structure have been obtained. Whenever both preliminary and final accounts of a given investigation have appeared in print, reference is given only to the latter. In some instances references are made to published abstracts of papers presented at the meetings of the International Union of Crystallography and of the American Crystallographic Association, and to declassified documents of the U. S. Atomic Energy Commission.

RESULTS OF NEUTRON DIFFRACTION

The 1950 *Annual Review of Physical Chemistry* gave a detailed discussion of the important work of Shull, Wollan, and collaborators on neutron diffraction in magnetic substances. Most of the results given in that review had not at the time been published, but appeared in print in the course of 1951. The results on neutron diffraction in paramagnetic and antiferromagnetic materials were reported by Shull, Strauser & Wollan (1), the results on ferromagnetic materials by Shull, Wollan & Koehler (2).

Last year's review also discussed other unpublished neutron diffraction results. Published accounts of these investigations have appeared as follows: UH_3 (3), ThC_2 (4), ThH_2 and ZrH_2 (5).

Shull & Wollan (6) have published an extensive and useful table of coherent scattering amplitudes as determined by neutron diffraction and transmission studies. This list comprises more than fifty nuclear species.

Structure of ammonium halides.—Results of neutron diffraction studies at liquid air and room temperatures on ND_4Cl have been reported by Goldschmidt & Hurst (7), and on ND_4Br by Levy & Peterson (8). At both temperatures the nitrogen and halogen positions correspond to those of cesium and chlorine in the CsCl structure, so that the main purpose of the investi-

¹ The survey of the literature pertaining to this review was concluded in January, 1952.

gations was the location of the deuterium positions. Both groups of investigators found that the deuterium atoms in the low temperature form are located on the body diagonals in accordance with the space group symmetry T_d^1 . Goldschmidt & Hurst give $N-D = 1.03 \pm 0.02 \text{ \AA}$ while Levy & Peterson find $N-D = 0.99 \pm 0.02 \text{ \AA}$. The vibration of the deuterium atoms about their equilibrium positions was found to be isotropic with a root mean square amplitude of 0.20 \AA in ND_4Cl and 0.14 \AA in ND_4Br .

The second order transformation from the low temperature to the room temperature form in the ammonium halides has been interpreted as the onset of free rotation (9) or of orientational disorder (10) of the ammonium ions. The former alternative is definitely ruled out by the neutron diffraction studies, but the two groups of investigators disagree as to the presence of orientational disorder. Goldschmidt & Hurst concluded from their observations that there was no positional disorder at room temperature. They found, however, that the vibration of the deuterium atoms was highly anisotropic, the motion being predominantly normal to the body diagonal as if there was torsional vibration of the ND_4 -group as a whole. A value of 18° is given as the root mean square angular amplitude. Levy & Peterson found the best agreement with their observations for a model with the orientational disorder suggested by Frenkel (10) and with the same type of torsional vibration of the ND_4 ion as found by Goldschmidt & Hurst in the chloride. The root mean square angular amplitude is given as 10° by Levy & Peterson. There is no valid reason for supposing that the situation is different for the two halides in the room temperature form, and it must accordingly be concluded that one of the two groups of investigators has misinterpreted the observations. It seems to this reviewer that the model presented by Levy & Peterson is the more likely one. In the first place the experimental data used by the Oak Ridge team contained many more reflections sensitive to positional disorder than was true of the Chalk River data. Secondly, it is inconceivable not to have positional disorder when the ND_4 ions execute torsional oscillations with such a large mean amplitude as is experimentally found.

Single crystal studies.—So far all structural studies using neutron diffraction have been confined to the powdered crystal method. Since the width of a powder reflection is about 1° the resolving power is poor, and one has accordingly been restricted to a study of simple structures with high symmetry. If neutron diffraction effects in single crystals are studied there is no problem with respect to resolving power, and there is hence no inherent reason why complex and low-symmetrical structures cannot be tackled by neutron diffraction. As is well known, neutron diffraction is a specific structural tool for the study of magnetic structures, for the location of light atoms in the presence of heavy ones, and for the differentiation between atoms of nearly equal atomic number. However, neutron diffraction used in conjunction with x-ray diffraction represents a much more powerful structural tool than x-ray diffraction or neutron diffraction alone. For many complex structures a comparison of neutron and x-ray structure factors will give valuable infor-

mation greatly facilitating the structure determinations. The neutron flux available in the experimental piles at Argonne, Brookhaven, Chalk River, Harwell, Oak Ridge, and Oslo is sufficient to make possible neutron diffraction studies of single crystals of about 1 mm. linear dimensions. Under these circumstances it is indeed surprising that the use of single crystal techniques in neutron diffraction studies has been so long delayed.

The problem of the effect of extinction in neutron diffraction was studied theoretically by Bacon & Lowde (11) some years ago. These workers used the equations of the theory of x-ray diffraction in mosaic crystals (12, pp. 159-76) and set the linear absorption coefficient equal to zero as is appropriate in most instances for neutrons. On the basis of a detailed analysis of the equations, Bacon & Lowde concluded that the crystal thickness had to be 0.01 cm. or less if extinction effects were to be negligible. It seems that Bacon & Lowde were a little too pessimistic in their numerical estimate of the effect of extinction, but their theoretical conclusions have otherwise been experimentally confirmed by Bacon (13) and by Peterson & Levy (14). It is found by direct experiment that extinction is not important, except in notoriously perfect crystals, if the mean thickness of the crystal parallel to the incident beam is of the order of 0.1 cm. or less. Peterson & Levy find virtually no extinction for 0.1 to 0.2 cm. thick crystals of NaCl, KCl, KHF_2 , and NH_4Cl . However, they observe considerable extinction in fluorite, calcite, and lithium fluoride crystals of the same thickness.

ANOMALOUS TRANSPARENCY OF PERFECT CRYSTALS

When an x-ray beam traverses a crystal in such a direction that a reflected beam is produced, one normally observes an increase in the absorption owing to the diversion of energy from the incident to the reflected beam. Borrmann (15) was the first to observe that some crystal specimens showed an anomalous behavior in that they were singularly transparent to a beam of x-rays entering the crystal so as to produce reflection from an internal lattice plane. The first quantitative measurements of the phenomenon were made by Borrmann (16) using calcite crystals. The effect is, indeed, striking. In a specific case described by Borrmann the transmitted x-ray beam has an intensity 10^{19} times greater than calculated from the usual absorption formula. Further experimental studies of the effect were reported during the past year by Campbell (17), who used an experimental technique somewhat different from Borrmann's.

Neither Borrmann nor Campbell seemed to be aware of the fact that their striking observations are in quantitative agreement with the theory of x-ray diffraction in absorbing perfect crystals (12, pp. 135-47). The pertinent equations are readily modified so as to fit the particular experimental set-ups used by Borrmann and by Campbell. In this manner theoretical expressions for the effective absorption coefficient as function of the crystal thickness have been deduced and compared with the experimental results (18). The normal linear absorption coefficient of calcite for x-rays of wave

length 1.54 \AA is 193 cm^{-1} . The values of the effective absorption coefficient measured by Borrmann and by Campbell for various values of the crystal thickness t_0 and those calculated from the theory are shown in Table I. As illustrated in Table I, there is excellent agreement between experiment and theory.

TABLE I
VALUES OF THE EFFECTIVE ABSORPTION COEFFICIENT

t_0	Theoretical	Observed	Observer
0.040 cm.	79 cm^{-1}	86 cm^{-1}	Campbell
0.212	30.5	30.2	Borrmann
0.271	28.6	27.7	Borrmann

The physical interpretation of the phenomenon is as follows. In the x-ray wave length region the absorption coefficient of the crystal medium cannot be regarded as constant, but must be considered as a periodic function of position and can hence be expressed as a Fourier series. In the ordinary transmission case, when no reflected beam is produced, the absorption coefficient of the single wave within the medium is given by the constant term μ_0 in this Fourier series. If on the other hand the incident beam enters at the exact Bragg angle and produces reflection in an internal lattice plane, the incident beam (and also the reflected beam) splits into two components. The absorption coefficients of the two components are $\mu_0 \pm \mu_H$, where μ_H is the Fourier coefficient associated with the reflecting lattice plane. In the case of reflection from the internal cleavage plane of calcite μ_H is only 10 per cent smaller than μ_0 . Hence, one component of the incident beam has an absorption coefficient $1.9 \mu_0$ and the other $0.1 \mu_0$. For a thick crystal the effective absorption coefficient is thus approaching the value $\mu_0 - \mu_H$ as the thickness increases. In a crystal which is so thin that it lets through the major part of both components there is clearly no anomalous transparency. Thus the phenomenon is observable only in crystals showing a high degree of perfection. Indeed, the anomalous transparency offers a sensitive method for measuring the degree of perfection in a crystal specimen. It should be mentioned that the effect is not restricted to x-rays, but is also possible with electrons and neutrons under the proper conditions of coherent absorption, crystal thickness, and crystal perfection.

INTERPRETATION OF X-RAY DIFFRACTION DATA

In the two previous volumes of the *Annual Review of Physical Chemistry* considerable space was devoted to a discussion of the various methods of interpreting x-ray diffraction data which have been developed in the postwar years. These methods fall into one of two main classes: (a) the determination of the phases of the coefficients in the Fourier series representing the electron

distribution function of the structure and (b) the deciphering of its Patterson synthesis. Both types of methods have been used successfully during the past year to determine complex crystal structures. The promising method of unraveling the Patterson synthesis by means of "image seeking functions" was described in last year's review; however, a detailed account of the new method appeared during the year (19).

Several new methods for the determination of complex crystal structures have been proposed in the course of 1951. From the mathematical point of view the most interesting new approach to the problem is that which comes from Hauptman & Karle (20). These workers interpret the structure factor equations as coupled closed-vector polygons. This interpretation permits the application of the solution of the random-walk problem to yield the probability distribution of the magnitudes of the structure factors and of the magnitudes of the vector separations of the atomic centers. Unobservable quantities like the phases of the structure factors are intentionally left out of consideration in the treatment. While the approach of Hauptman & Karle is of fundamental character, it is not clear as of this writing whether or not this highly interesting point of view may lead to a practical method for solving complex crystal structures.

What promises to be a useful analytical method for the solution of centrosymmetrical structures with many degrees of freedom has been developed by Sayre (21), by Cochran (22), and by Zachariasen (23). Sayre considered a crystal composed of like atoms and studied the similarity between the electron density function and its square. On this basis Sayre has deduced a new set of relationships between structure factors. Cochran examined the extent to which a partial Fourier series, which contains as coefficients only some of the larger structure factors, will represent the electron density in a crystal structure. By means of this method of approach and the use of Sayre's equations, Cochran obtained a probable relation between the signs of structure factors. Zachariasen started out with an identity relation between structure factors and ended up with the same probable relationship between signs of structure factors as Cochran. In spite of the widely divergent starting points, the final conclusion of the three workers is the same. This may be expressed as the probable validity of the equation $S_H S_K = S_{H+K}$ where S_H , S_K and S_{H+K} denote the algebraic signs of the structure factors F_H , F_K and F_{H+K} corresponding to three strong reflections. When the method of inequalities offered by Harker & Kasper (24) leads to information about structure factor signs, the result is expressed in the form $S_H S_K = S_{H+K}$ with the validity of the equation assured. If there are many degrees of freedom in the structure very few such valid equations can be obtained, and one must then make use of the fact demonstrated by Sayre, Cochran, and Zachariasen that relations $S_H S_K = S_{H+K}$ as applied to strong reflections are probably, but not necessarily, correct. The task of determining the amplitude signs for the strong reflections is thus reduced to a self-consistency problem with respect to this probable relationship between signs. Using this self-consistency

method, which clearly is an extension of the method of inequalities to more complicated structures, Sayre in the case of hydroxyproline, and Cochran in the case of glutamine, succeeded in establishing enough structure factor signs to yield a good approximation to a two-dimensional Fourier projection of the structure. Zachariasen applied the method to the three-dimensional structure of monoclinic metaboric acid and determined 200 amplitude signs making possible a three-dimensional Fourier synthesis which gave a direct determination of the 27 parameters for boron and oxygen atoms. The promise of the new method is illustrated by the fact that the three structures to which it was successfully applied could not be solved by the method of inequalities.

McLachlan & Harker (25) have proposed a method of finding the signs of structure factors for centro-symmetrical crystals from the shifted Patterson product. Their suggestion has not as yet been tested as to practical feasibility.

RESULTS OF X-RAY DIFFRACTION STUDIES

Elements, metals, and intermetallic compounds.—Burbank has determined the crystal structure of both the alpha (26) and beta form (27) of monoclinic selenium. The alpha form contains eight-membered puckered rings similar to those observed in orthorhombic sulphur by Warren & Burwell (28). The Se—Se distance in the ring is 2.34 Å and the covalent bond angle is 105°. The closest separation of selenium atoms belonging to different molecules is 3.53 Å. In the beta form the selenium molecule is an eight-membered chain with the configuration of a puckered-ring molecule in which one of the bonds is broken. The Se—Se distances within a chain vary between 2.21 Å and 2.42 Å while the distance across the "broken bond" is 3.04 Å. The bond angles within the chain range from 103° to 125°. Intermolecular distances are as low as 2.85 Å.

A new allotropic form of beryllium metal was reported (29) during the past year. To put the record straight it should be stated that the information was incorrect (30).

New results have been obtained on the structure of elements at the end of the periodic system, namely for protactinium metal, the beta form of uranium metal and for neptunium metal. Tucker (31) has described an approximate structure of beta uranium which is the form stable in the range 660–760°C. The work was done with the aid of a single crystal stabilized at room temperature by the addition of a small amount of chromium. The crystals are tetragonal with $a_1 = 10.52$ Å, $a_3 = 5.57$ Å and contain 30 atoms in the unit cell. Tucker reported the space group as $P4nm$ and proposed a structure with six distinct types of uranium atoms with a total of 12 parameters for which he gave approximate values. It has been found by Kasper *et al.* (32, 33) and by Bergman & Shoemaker (34, 35) that the sigma phase in the systems Co—Cr and Fe—Cr has a structure similar to that of β -U. These workers found, however, that the space group for the sigma phase compounds is

P4/mnm, and that hence there are only five types of distinct atoms and only seven instead of 12 parameters. It is unlikely that the space group for β -U is also P4/mnm. Only small changes in Tucker's z-parameter values are needed in order to raise the space group symmetry, but these changes seem well within the limits of error of Tucker's intensity measurements. Table II gives Tucker's values for the z-parameters and the idealized values corresponding to the space group P4/mnm. Unfortunately Tucker's parameter determination is not accurate enough for a detailed consideration of the interatomic distances and binding. However, it seems to be true that each uranium atom, as in α -U, forms a small number (usually four) of short bonds with U—U distances in the range 2.7–2.9 Å.

The structure exhibited by protactinium metal (36) is also unique, but of a very simple type easily deduced from powder diffraction patterns of micro-

TABLE II
PARAMETERS FOR β -U

Atomic Positions	Tucker's Values	Idealized Values
2(a)	0.66	3/4
4(c)	0.23	1/4
4(c)	0.00	0
4(c)	0.50	1/2
8(d)	0.25	1/4
8(d)	0.20	1/4

preparations. The structure is tetragonal body-centered with two atoms in the unit cell of dimensions $a_1 = 3.925$ Å, $a_3 = 3.238$ Å and a density of 15.37 gm./cc. Each protactinium atom has ten neighbors, eight at a distance of 3.21 Å and two at 3.24 Å. The metallic radius (for co-ordination number 12) is 1.63 Å, and this is interpreted as evidence that all five valence electrons participate in the binding, and that hence there are no 5f electrons in the metal.

A unique structure has been found also for the room temperature form of neptunium (37). The structure was deduced from powder diffraction patterns of micro-samples of the metal. The orthorhombic unit cell contains eight atoms, falling into two distinct types, and the calculated density is 20.45 gm./cc. The determination of the four parameters led to a structure which may be regarded as a heavily distorted cubic body-centered structure. As in the α -U structure (38) each metal atom in the α -Np structure forms four short bonds. The bond distance is 2.63 Å as compared with 2.80 Å in α -U. The observed bond length indicates that six to seven electrons per atom participate in the formation of the four short bonds. It is accordingly concluded that there is at most one 5f electron per neptunium atom in the metal. The directions of the four short bonds are quite different for the two

kinds of neptunium atoms in the structure. The results obtained for α -U, β -U and α -Np indicate that the existence of strong covalent bonds is a characteristic feature in the structure of the metals at the end of the periodic system. These elements exhibit "normal" metal structures only at temperatures near the melting point.

A detailed structural study of the ζ phase in the Ag—Zn system has been published by Edmunds & Qurashi (39). Tang & Pauling (40) have studied the structure of alloys of lead and thallium. From a careful study of the variation of the lattice constant with composition in the cubic close-packed range from 0 to 87.5 atomic per cent thallium, strong indication is obtained for the existence of ordered structures PbTl_3 and PbTl_7 . A theory of the structure of the alloys is presented which explains the observed phase diagram, and which in particular accounts for the existence of a maximum melting point at 63 atomic per cent thallium.

A number of compounds of 4f and 5f elements with other metals or with semimetals have been investigated. Amalgams of La, Ce, Pr, and Nd of the composition MeHg were examined by Iandelli & Ferro (41). The dimension of the cubic body-centered cell is found to be anomalously small for the cerium compound as compared with the other compounds of the series. This observation is further evidence that cerium in many metallic type structures must be assigned more than the three valence electrons characteristic of most of the 4f elements. Rundle *et al.* have continued their extensive studies of the alloy systems of thorium and uranium with transition elements. The most recently reported results are for the Th—Mn system (42). The existence of the intermetallic compounds ThMn_2 , $\text{Th}_6\text{Mn}_{23}$, and ThMn_{12} has been established and their structures are described. LaSi_2 , PrSi_2 , NdSi_2 , and SmSi_2 are reported (43) to have the ThSi_2 type of structure previously found for CeSi_2 , USi_2 , NpSi_2 , and PuSi_2 (44). The crystal structure of CeB_4 , ThB_4 , and UB_4 has been described by Zalkin & Templeton (45). The boron atoms form a three-dimensional network with B—B distances in the range 1.69 to 1.80 Å, each metal atom being bonded to 18 boron atoms. Pu_2C_3 (the compounds U_2C_3 and Np_2C_3 are isostructural) is reported (46) to have a cubic structure containing C_2 -groups.

Crystal chemistry of technetium.—The crystal structure of technetium metal was described some years ago (47). Some results on the identification and crystal structure of compounds of technetium were reported during the year (48). TcO_2 , and also ReO_2 , are reported to be monoclinic and isostructural with MoO_2 . TcS_2 and ReS_2 are said to have a disordered structure related to the MoS_2 type. K_2TcCl_6 has the K_2PtCl_6 type of structure. NH_4TcO_4 , KTcO_4 , and AgTcO_4 all have the scheelite type of structure. These results show that technetium is closely similar to rhenium in crystal chemical respect, the crystal radius of Tc being 0.01 Å smaller than the Re radius for corresponding valence state and binding.

Crystal chemistry of protactinium.—During the past year the identification and crystal structure of a number of protactinium compounds were re-

ported (49, 50). It was found that the normal valence is four and five, the two states being of equal prominence in solids. Attempts to prepare trivalent compounds were unsuccessful, showing that the designation of protactinium as an actinide element is inappropriate.

The study of the system $\text{PaO}_2\text{—Pa}_2\text{O}_5$ is of specific interest. The protactinium oxide obtained by ignition in air has an approximate composition of $\text{PaO}_{2.25}$ and is not Pa_2O_5 as has been reported (51). The dioxide can be prepared by treating the ignition product with hydrogen at 1400°C ., and the pentoxide by treatment with oxygen at 1100°C . PaO_2 has the fluorite type of structure with $a = 5.505 \text{ \AA}$. As the oxygen content increases, the unit cell edge decreases to $a = 5.416 \text{ \AA}$ at Pa_2O_5 . The interstitial oxygen atoms tend to go into preferential sites, and heat treatment produces a tetragonal form of approximate composition $\text{PaO}_{2.2}$. The normal form of Pa_2O_5 is orthorhombic and isostructural with U_2O_5 , Nb_2O_5 , and Ta_2O_5 . Other compounds whose crystal structures are known are PaF_4 with the ZrF_4 type of structure, PaCl_4 isostructural with UCl_4 , PaOS with PbFCl , PaH_3 with UH_3 , and PaO with NaCl .

The structural results show that protactinium in the metal (36) and in pentavalent compounds behaves in crystal chemical respect as a homologue of niobium and tantalum. In tetravalent compounds on the other hand protactinium must be regarded as a "thoride" element with one $5f$ electron and with a crystal radius intermediate between that of thorium and that of tetravalent uranium.

Acids and hydrogen compound.—During the past few years a number of structure determinations using single crystals have been carried at low temperatures. This work has been made possible by the development of simple techniques for the preparation and manipulation of small single crystals at temperatures down to liquid air temperature. During the x-ray exposure the single crystal can be maintained indefinitely at a constant low temperature by means of a cold air stream. The experimental techniques have been described by Bouttier (52), Luzatti (53), Collin & Lipscomb (54), and by Post, Schwartz & Fankuchen (55).

Using these low temperature techniques Luzatti has determined the structures of HNO_3 (53), $\text{HNO}_3 \cdot \text{H}_2\text{O}$ (56), and $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ (57). The former two structures were discussed in last year's review, but the detailed accounts of the investigations appeared during the past year. In the trihydrate the bond lengths and the bond angles within the NO_3 -group are essentially the same as found in the monohydrate and in the anhydrous form, but the nitric acid and water molecules are involved in an intricate three-dimensional net of hydrogen bonds. The oxygen atoms of two of the water molecules are bound by three hydrogen bonds, orientated along the edges of a trigonal pyramid. The oxygen of the third water molecule is surrounded tetrahedrally by four hydrogen bonds, as in the structure of ice.

Dulmage & Lipscomb (58) investigated the crystal structure of HCN both above and below the transition point at -102.8°C . The high tempera-

ture form is tetragonal with $a_1 = 4.63 \text{ \AA}$, $a_3 = 4.34 \text{ \AA}$. In both forms there are two molecules per unit cell, and the crystal structure consists of infinite linear chains, all pointing in the same direction, with the molecules along the a_3 -axis. The bond distances within the molecule are known with greater accuracy from microwave analysis (59) than could be obtained by x-ray analysis. The microwave values are $\text{C—N} = 1.157 \text{ \AA}$ and $\text{C—H} = 1.061 \text{ \AA}$. Using $\text{C—N} = 1.16 \text{ \AA}$ the hydrogen-bond distance ($\text{C—H} \dots \text{N}$) is 3.18 \AA in both forms.

Three forms of metaboric acid, HBO_2 , are known to exist. In the orthorhombic form (60) the structure contains groups $\text{B}_3\text{O}_6^{3-}$ as previously found in the structure of KBO_2 (61). The B_3O_6 -groups are bonded together by hydrogen atoms with $\text{O—H} \dots \text{O} = 2.74 \text{ \AA}$ so as to form infinite layers which are 3.12 \AA apart. A preliminary structure has been reported for the monoclinic form of HBO_2 (23). The boron and oxygen atoms are bonded together to form endless chains. The constituents of the chains are BO_4 -tetrahedra and B_2O_5 -groups, a B_2O_5 -group being composed of two BO_3 -triangles having a corner in common. The mean B—O distance is 1.36 \AA in the triangular and 1.46 \AA in the tetrahedral configurations. The hydrogen atoms provide bonding between chains, the hydrogen bond distance $\text{O—H} \dots \text{O}$ being on the average 2.69 \AA .

The crystal structure of anhydrous selenic acid, H_2SeO_4 , has been determined by Bailey & Wells (62). The orthorhombic structure contains tetrahedral SeO_4 -groups, each joined by four $\text{O—H} \dots \text{O}$ bonds to four neighboring groups to form puckered layers. The mean bond length Se—O is 1.61 \AA and the lengths of the $\text{O—H} \dots \text{O}$ bonds are 2.61 \AA and 2.68 \AA .

A structural study of hydrazine (54), N_2H_4 , at -40°C . led to a monoclinic structure with two molecules in the cell. The N—N distance in the molecule was found to be 1.46 \AA and the smallest non-bonded $\text{N} \dots \text{N}$ distances 3.19 \AA , 3.25 \AA and 3.30 \AA . The hydrogen atoms could not be conclusively located, but the suggested location of the hydrogen atoms gives the molecule an eclipsed configuration instead of the staggered one usually assumed.

The structure of hydrogen peroxide has been reported by Abrahams, Collin, & Lipscomb (63), who studied single crystals at -20°C . The O—O bond distance was found to be 1.49 \AA and the angle between the O—O and O—H bonds 97° . The azimuthal angle between planes containing the hydrogen bonds and the O—O bond is given as 94° . Each oxygen atom has two close approach distances of 2.78 \AA which are interpreted as $\text{O—H} \dots \text{O}$ bonds.

Nitta, Sakurai & Tomiie (64) have determined the structure of the orthorhombic form of hydrazonium sulphate. The usual bond distance of $\text{S—O} = 1.49 \text{ \AA}$ is found in the tetrahedral sulphate group while O—O distances between different sulphate groups are all greater than 3 \AA . The hydrazonium ion may be considered to be of the *trans* type with $\text{N—N} = 1.40 \text{ \AA}$. One of the nitrogen atoms forms three hydrogen bonds with the $\text{N—H} \dots \text{O}$ distance $2.73\text{--}2.77 \text{ \AA}$, and the other may be regarded as forming three bifurcated hy-

drogen bonds with distances 2.79–2.99 Å. Besides the oxygen atoms linked by hydrogen bonds, each $\text{N}_2\text{H}_6^{++}$ group has three more oxygen neighbors with $\text{N} \cdots \text{O} = 2.78\text{--}2.89$ Å.

The crystal structure of pentaborane, B_5H_9 , has been determined by Dulmage & Lipscomb (65), while Hedberg, Jones & Schomaker (66) have studied the molecular structure in the gaseous state by electron diffraction. There is excellent agreement between the results of the two investigations. The pyro-electric crystals of B_5H_9 are tetragonal with two molecules per cell and space group symmetry $I4mm$. The five boron atoms form a tetragonal pyramid. The B—B distance is 1.77 Å in the base of the pyramid and 1.66 Å along the slanting edges of the pyramid. One hydrogen atom is covalently bonded to each of the five boron atoms with B—H = 1.20 Å. The four remaining hydrogen atoms form "bridge bonds" between the boron atoms at the base of the pyramid, the B—H distance in the bridge bonds being 1.35 Å. The closest intermolecular approaches are between hydrogen atoms and range from 2.46 to 2.96 Å.

Halogen compounds.—Hoard and co-workers have made detailed structural studies of four related boron trifluoride addition compounds, namely $\text{H}_3\text{CH}_2\text{N-BF}_3$ (67), $\text{H}_3\text{CCN-BF}_3$ (68), $\text{H}_3\text{N-BF}_3$ (69), and $(\text{H}_3\text{C})_3\text{N-BF}_3$ (70). A comparison of the results for the four compounds (71) shows the following bond distances and bond angles:

N—B	1.57–1.60 Å
B—F	1.33–1.39
F—F	2.23–2.27
N—F	2.34–2.46
N—CH ₃	1.50
$\angle \text{F—B—F}$	107–114°
$\angle \text{F—B—N}$	103–112°
$\angle \text{B—N—C}$	105–114°
$\angle \text{C—N—C}$	114°

The B—N bond distances are about 0.1 Å greater than the sum of the covalent radii. The increase in the B—F separation as compared with the value B—F = 1.30 Å in BF_3 is attributable to the increase in coordination number from three to four.

Gutman & Jack (72, 73) have shown that MoF_3 and TaF_3 have the ReO_3 type of structure whereas the structure of VF_3 is similar to that of AlF_3 . The bond distances within the octahedral XF_6 groups are given as V—F = 1.94 Å, Mo—F = 1.95 Å, and Ta—F = 1.95 Å. The trifluorides of yttrium, of the 4f elements Sm to Lu, and of bismuth have been found to be isostructural (74), the structure being similar to that of cementite. It should be mentioned at this point that the structure ascribed to BiF_3 by Hassel & Nilssen (75) is erroneous since the compound they investigated was not BiF_3 , but Bi_2OF_4 (76). Oxyfluorides, XOF , of yttrium, of the 4f elements and of the 5f elements are shown (77) to have deformed fluorite types of structure. The deformation is caused by ordering of the oxygen and fluorine atoms which in turn is due to the considerable difference between X—O and X—F distances.

BeCl_2 (78) has been found to have the silicon disulfide structure. Thus BeCl_4 tetrahedra are linked together by shared edges into infinite chains. The Be—Cl distance is 2.05 Å, which corresponds well with the value calculated from covalent as well as ionic radii. The bond angle Be—Cl—Be is 82° . Closest Cl—Cl distance between different chains is 3.85 Å. Schulz (79, 80) has studied the structure and orientation of thin films of alkali and thallium halides deposited by evaporation on single-crystal substrates. He found that CsCl , CsBr , CsI , TlCl , TlBr , and TlI could be deposited with the NaCl type of structure (rather than with the normal CsCl type of structure) by proper choice of the substrate. The unit cell constants for the NaCl type of structure were found to be:

Compound	<i>a</i>
CsCl	6.94 Å
CsBr	7.23
CsI	7.66
TlCl	6.30
TlBr	6.58
TlI	6.94

In the structure of NaAlCl_4 (81) there are tetrahedral ions AlCl_4^- . Each sodium atom has seven chlorine neighbors at distances 2.79–3.29 Å. The distance Al—Cl = 2.13 Å is shorter than the sum of the covalent radii, but is in agreement with the distance calculated for ionic binding.

ThBr_4 has been shown (82) to have the UCl_4 -type of structure (83), K_2ReBr_6 (84) the K_2PtCl_6 type. InBr (85) has a layer structure like that of TlI . Each In atom has five Br neighbors at the corner of a rectangular pyramid. One In—Br distance is 2.80 Å and four 3.29 Å.

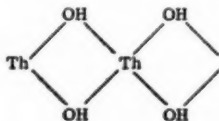
Nearly all of our present structural information on polyhalides is due to work carried out by Mooney during the 1930's (86, 87, 88, 89). Mooney found I_3^- , ICl_2^- , and IClBr^- to be linear groups while ICl_4^- had a planar square configuration. During the past year Hach & Rundle (90) have described the structure of tetramethylammonium penta-iodide. The structure exhibits nearly square iodine nets (planar to ± 0.64 Å) within which V-shaped I_5^- ions can be distinguished. The angle of the V is 94° , the arms being linear within 4° . I—I distances within the ion are 2.93 Å and 3.14 Å as compared with 2.67 Å in I_2 . The I_5^- ion may be described as an I^- ion to which two I_2 -molecules are attached. In this interpretation the I_2 distance is 2.93 Å and I—I^- is 3.14 Å. Other iodine-iodine distances within the net are 3.55 Å or greater, while the nets are 4.3 Å apart.

Oxides, oxygen compounds, minerals.—The crystal structure of SO_2 has been investigated by Kanda & Sugawara (91) and by Post, Schwartz & Fankuchen (92). The two groups of workers found the same structure with S—O = 1.43 Å and sulfur bond angle of 120° . The $\text{S} \cdots \text{O}$ distances between different molecules exceed 3.1 Å. The observed bond distance and bond

angle are in agreement with the more accurate values $\text{S—O} = 1.433 \text{ \AA}$ and $\text{O—S—O} = 119.5^\circ$ deduced from microwave analysis (93). Frueh (94) has determined the structure of As_2O_3 in the form of the monoclinic mineral claudetite. As in the gaseous molecule and in the cubic crystalline form, each arsenic atom is bonded to three oxygen atoms with $\text{As—O} = 1.80 \text{ \AA}$ and bond angles of about 97° at the arsenic atom. The arsenic and oxygen atoms link together to form irregular sheets parallel to the perfect cleavage. The mineral anosovite, Ti_2O_5 , containing both tetravalent and trivalent titanium atoms, has been shown (95) to be isomorphous with pseudo-brookite, Fe_2TiO_5 . As part of systematic studies of double oxides Aurivillius (96) has reported on the crystal structure of BiNbO_4 , BiTaO_4 , and BiSbO_4 .

The crystal structure of NaNO_2 , originally determined by Ziegler (97), has been re-examined by Truter (98) and by Carpenter (99) in order to obtain accurate results for the dimensions of the nitrite group. Ziegler found $\text{N—O} = 1.13 \text{ \AA}$ and $\angle \text{O—N—O} = 1.32^\circ$. These values are confirmed by Truter, whereas Carpenter obtained $\text{N—O} = 1.23 \text{ \AA}$ and $\text{O—N—O} = 116^\circ$. Thus the new investigations have increased the need for a careful re-examination.

PO_4 -tetrahedra are linked into four-membered rings in $(\text{NH}_4)_4\text{P}_4\text{O}_{12}$ (100). Infinite chains of VO_4 -tetrahedra, analogous to the chains in some metasilicates, are observed in NH_4VO_3 (101), while vanadium is bonded to five oxygen atoms at distances $1.54\text{--}2.02 \text{ \AA}$ in V_2O_5 (102). Zigzag chains $\text{Th}(\text{OH})_2$ of the type



have been found both in $\text{Th}(\text{OH})_2\text{CrO}_4 \cdot \text{H}_2\text{O}$ (103) and $\text{Th}(\text{OH})_2\text{SO}_4$ (104).

Structural results have been reported for many minerals, such as quen-selite (105), malachite (106), lanarkite (107), ludlamite (108), iron lazulite (109), bandylite (110), and boracite (111). A re-examination of the tourmaline structure (112) has led to more reasonable interatomic distances than those reported by Donnay & Buerger (113). Thorium silicate, ThSiO_4 , which has long been known in nature as the mineral thorite with the zircon structure, has now been observed as the new mineral huttonite (114), which has the monazite type of structure.

Organic structures.—A most excellent review of crystal structure results for organic compounds covering the four years 1947 to 1950 has recently been published (115). A number of crystal structure papers dealing with organic compounds have appeared during the year, chiefly in *Acta Crystallographica*. The main goal of nearly all of these investigations was the determination of the molecular structure, and the results obtained are therefore discussed in the chapter, "Experimental Molecular Structure."

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EXPERIMENTAL MOLECULAR STRUCTURE¹

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This report on the structures of molecules for the year 1951 includes the results of investigations leading to the evaluation of interatomic distances in molecules, and in a few cases, results dealing only with intramolecular configurations.

Spectroscopic results still afford the highest precision when sufficient data are available to avoid assuming values for interatomic distances provided by other methods of investigation. The precision attainable in frequency determinations in the microwave region is illustrated in the tabulation with seven significant figures of frequencies for rotational transitions in the 2 to 3 mm. region for specified isotopic species of O₂, CO, OCS, N₂O, NF₃, PF₃, POF₃, PSF₃, CH₃F, CH₃CCH [Johnson, Trambarulo & Gordy (1)]; the lower precision in the structural information based on such data was discussed in the 1951 *Review of Physical Chemistry* [Roth (2)]. Reports giving only the assignment of frequencies without an evaluation of moments of inertia or interatomic distances are not included in this review.

All electron diffraction data from gases are included, although the variations in the precision claimed will be noted. Most of the data published in 1951 were obtained by the visual examination of the electron diffraction negatives, some of the results being based on observations not reaching as far as s values (equal to $4\pi(\sin \theta/2)/\lambda$) of 20 while other sets of data reach beyond 30. Two additional laboratories have started the use of rotating sectors placed before the negative during the exposure and of recording microphotometers for measuring the sectorized negatives.

X-ray diffraction results from crystals are included for substances showing well defined molecules in the solid state, when the data reported include a determination of atomic positions affording interatomic distances with uncertainties not larger than about 0.05 Å. The interesting questions of the interactions between molecules, related to packing arrangements or the formation of hydrogen bonds, are excluded from this review.

Neutron diffraction has been applied to the determination of interatomic distances in a gaseous substance for the first time. Alcock & Hurst (3) report a CF distance of 1.33 Å in CF₄ compared with the electron diffraction value of 1.36 Å (4), the difference of 0.03 Å lying within the experimental error of the neutron diffraction method. Other gases studied by the same authors (5, 6) include N₂, CH₄, D₂, O₂, and CO₂. In all of these cases the primary interest lay in the scattering process itself and led to determinations of the ratio of coherent to total scattering rather than of the interatomic distances. The use of gas pressures of several atmospheres required to increase the total

¹ This survey of literature pertaining to this review was concluded in December, 1951.

scattering introduces intermolecular interference effects apparent at low scattering angles. The limited range in s for which scattering data can be obtained with neutrons having a wave length long enough to show appreciable scattering, limits the applicability of this method for determining structures in gas molecules.

Neutron diffraction has been used by Goldschmidt & Hurst (7) on solid ND_4Cl at -180° and at room temperature. The ND distance shifts from $1.03 \pm 0.02 \text{ \AA}$ at the lower temperature to about 0.97 \AA at the higher temperature although the authors caution that no analysis has been made of the vibrations of the deuterons. They conclude that free rotation of the ND_4 ion does not occur at room temperatures.

STRUCTURES

Boron compounds.—The noncoplanar bridge model for B_2H_6 with D_{2h} symmetry, for which spectroscopic evidence originally was found by Price (8) in 1948, is further supported by the infrared absorption spectrum observed by Lord & Nielsen (9) for certain isotopic species in the liquid state at -130°C ., although the C_{2v} unsymmetrical two-proton-bridge model can not be definitely excluded. Bauer's (10) statement that certain features of his electron diffraction data on B_2H_6 were inconsistent with Price's bridge model led to a complete reinvestigation by Hedberg & Schomaker (11), who support the bridge model with BH distances in the bridge of 1.33 \AA , BH for the nonbridge hydrogen of 1.19 \AA , and a bridge angle at boron of 97° . For tetramethyl diborane spectroscopic data (12, 13) and electron diffraction data (14) agree on a two-proton bridge; the BB diagonal of the bridge is 1.84 \AA , 0.07 \AA larger than in diborane.

Hedberg, Schomaker & Jones (14) also reported on 1,1-dimethyl diborane, amino diborane and N-dimethyl aminodiborane. For the last of these there is strong evidence of a nitrogen replacement of one of the bridge hydrogen atoms with BN values of 1.55 \AA . BN bond lengths in coordination compounds of BF_3 have been observed in crystals by Hoard, Geller *et al.* The BN distances in H_3NBF_3 (15), $(\text{CH}_3)_2\text{H}_2\text{NBF}_3$ (16), $(\text{CH}_3)_3\text{NBF}_3$ (17), and CH_3CNBF_3 (18) are 1.60 \AA , 1.57 \AA , 1.59 \AA , and 1.64 \AA , respectively (19). In the methyl cyanide boron trifluoride complex the larger BN distance and the smaller BF distance (1.33 \AA as compared with $1.38\text{--}9 \text{ \AA}$ in the other three compounds) is correlated with the low chemical stability of this compound.

BCl bonds observed in BCl_3 and B_2Cl_4 by Hedberg, Schomaker & Jones (14) and in $\text{C}_6\text{H}_5\text{BCl}_2$ by Bauer & Coffin (20) agree at $1.72\text{--}3 \text{ \AA}$, while in B-trichloroborazole (20) the BCl distance is 1.78 \AA .

B_2H_9 has been reinvestigated by electron diffraction in the gas [Hedberg, Jones & Schomaker (21)] and by x-ray diffraction in the solid [Dulmage & Lipscomb (22)]. Both studies agree on a square pyramid but the dimensions of the molecule in the crystal with BB lengths of 1.77 \AA on the base of the

pyramid and 1.66 \AA along the slanting edge appear to be about 2 per cent shorter than in the molecule in the vapor.

For $\text{B}_{10}\text{H}_{14}$ a calculation (23) of electron diffraction intensity based on the Kasper, Lucht & Harker model described in the 1951 *Review of Physical Chemistry* (2) gives better agreement with the data than other models previously considered (24).

Silicon, germanium, and tin compounds.—Brockway & Bond (25) using the sector-microphotometer method of interpreting electron diffraction data observed SiC distances in mono-, di-, and tri-methyl silanes of $1.857 \pm 0.007 \text{ \AA}$, $1.860 \pm 0.004 \text{ \AA}$, and $1.873 \pm 0.007 \text{ \AA}$; the first two compounds appear to have shorter bonds than the third by about 0.01 \AA . Previous results (4) of 1.93 \AA and 1.90 \AA for the SiC bonds in tetramethyl silane and hexamethyl disilane call for a reinvestigation by the improved technique. A value of 1.88 \AA is reported by Sheridan & Gordy (26) for SiF_3CH_3 based on microwave results with the SiF_3 and CH_3 configurations assumed from other molecules.

The same authors (26) report SiF distances of not more than 1.563 \AA in SiF_3H , SiF_3Cl , and SiF_3Br , as compared with 1.59 \AA in SiH_3F (27). The decrease of 0.03 \AA ensuing from the mutual effect of the fluorine atoms is smaller than the 0.06 \AA decrease between CF in CH_3F and in CHF_3 ; and the difference is ascribed to the possibility of double bond formation in electronic structures contributing to the ground state of SiH_3F but not in CH_3F because of the limitation to four bond orbitals on carbon. It should be noted that the results in SiF_3H , SiF_3Cl , and SiF_3Br depend on the assumption of SiH equal to $1.55 \pm 0.05 \text{ \AA}$ in the first compound and of $\angle\text{FSiF}$ of $108.5 \pm 1^\circ$ in the other two. The SiCl and SiBr distances are shorter by 0.04 \AA than in the compounds SiH_3Cl and SiH_3Br . These results will be of special interest in comparison with the effect of fluorine substitution in methyl derivatives when complete determinations of structure not involving assumed parameter values are available.

Phenyl silane and dichlorophenylsilane (28) give electron diffraction sector data in agreement with previously determined structures.

Trisilylamine $(\text{SiH}_3)_3\text{N}$ has a coplanar configuration of the silicon atoms around the nitrogen with SiN distances of 1.73 \AA [Hedberg, Schomaker & Jones (14)]. The flattening of the pyramid observed for trimethylamine (4) may be due to the back coordination of the electron pair on nitrogen which is permitted by available orbitals on silicon but not on carbon.

From electron data germanium tetrafluoride has a tetrahedral structure with GeF bonds of $1.67 \pm 0.03 \text{ \AA}$ [Caunt, Mackle & Sutton (29)].

Several isotopic species of GeF_3Cl have been used in a microwave determination by Anderson, Sheridan & Gordy (30) to give the following results: GeF, $1.688 \pm 0.017 \text{ \AA}$; GeCl, $2.067 \pm 0.005 \text{ \AA}$; $\angle\text{FGeF}$, $107.7 \pm 1.5^\circ$. In view of the size of the central atom it is unlikely that the decrease of the FGeF angle below the regular tetrahedral value is due to the larger size of

chlorine compared with fluorine. Electron diffraction values for $\angle \text{FSiF}$ in SiF_3Cl (31) and for $\angle \text{FCF}$ in CF_3CCH (32) are $108.5 \pm 1^\circ$ and $107.5 \pm 1^\circ$, respectively. Current work on other CF_3X structures should help to determine whether trifluoro groups characteristically have bond angles smaller than 109.5° .

A microwave investigation (33) of methyl stannane, CH_3SnH_3 , gives a CSn distance of 2.14 \AA and SnH of 1.70 \AA with all bond angles assumed to be 109.5° and CH to be 1.090 \AA .

Other inorganic compounds.—Weiss & Strandberg (34) obtained microwave values for the effective bond lengths (including zero point vibrations) in NH_2D and NHD_2 : $1.008 \pm 0.004 \text{ \AA}$ and $1.016 \pm 0.008 \text{ \AA}$, compared with Herzberg's (35) average for NH_3 and ND_3 of 1.014 \AA .

Collin & Lipscomb (36) in an x-ray study of hydrazine at -15°C . and -40°C . report a crystal structure belonging to the space group C_{2h}^2 and having an NN distance of $1.46 \pm 0.02 \text{ \AA}$. Wagner & Bulgozdy (37) disagree on the basis of infrared and Raman investigations of the liquid at 60°C . and the solid at -190°C .; they conclude that the molecules in the solid state occur only in the *trans* configuration with symmetry C_{2h} , a result incompatible with the proposed space group since it provides no molecular sites with this point group symmetry. The liquid is an equilibrium mixture of *trans* and one pair of *gauche* (C_2) configurations.

Nitric oxide forms a dimer in the vapor at temperatures down to -180°C . as shown by its absorption in the ultraviolet region [D'Or, deLattre & Tarte (38)], in the liquid and solid according to the Raman and infrared spectra [Smith, Keller & Johnston (39)], and in the solid by x-ray results reporting short NO distances of 1.10 \AA and long distances of 2.38 \AA in a tetra-atomic coplanar molecule [Dulmage, Meyers & Lipscomb (40)].

The spectrum of nitrous acid has been investigated in the 2 to 25μ region. The existence of isomers reported by D'Or & Tarte (41) on the basis of the observed doubling of adsorption bands is supported by Jones, Badger & Moore (42), who made frequency assignments. They evaluate parameters for *cis* and *trans* isomers in a molecule with the formula HONO and evidently find no evidence for the tautomeric form with hydrogen on the nitrogen atom as discussed by Sidgwick (43). The *cis* form has the higher energy by $506 \pm 250 \text{ cal. per mole}$. The bond distances determined from the frequencies with the aid of Badger's rule (44) are: HO , 0.98 \AA ; ON , 1.46 \AA ; NO , 1.20 \AA .

In NOCl the NO distance has been measured by electron diffraction at 1.14 \AA with NCl at 1.95 \AA [Ketelaar & Palmer (45)]. Infrared (46) and microwave (47) spectra now support these values. Evidently the substitution of OH increases the NO bond by 0.06 \AA and drops the NO frequency from 1844 cm^{-1} to 1696 cm^{-1} .

Anhydrous nitric acid and the monohydrate have been studied by x-ray crystal structure methods [Luzzati (48, 49)]. In the anhydrous acid the short NO distance (1.24 \AA) agrees with the electron diffraction value [Maxwell & Mosley (50)], but the NO bond to the oxygen holding the hydrogen

atom is 1.30 Å in the solid and 1.41 Å in the vapor. While the precision of these values is not great, the difference is in the direction expected for the effect of hydrogen bond formation in the solid. The hydrated acid shows nearly trigonal symmetry in the NO_3 group with an average NO distance of 1.24 Å.

Loomis & Strandberg (51) report bond distances in PH_2D , AsH_2D , and SbH_2D of 1.419 Å, 1.523 Å, and 1.712 Å, respectively, in combining their microwave data with infrared data on the more abundant isotopic species. The bond angles (91.5° to 93.5°) are 5° smaller than the infrared values.

The crystal structure of hydrogen peroxide shows an OO distance of 1.49 ± 0.02 Å with a dihedral angle of 94° [Abrahams, Collin & Lipscomb (52)].

Two microwave reports on SO_2 (53, 54) lead to the evaluation of three moments of inertia. Two of these are sufficient to fix the molecular structure, and the results depend on which pair is used. The moments I_a and I_b give an SO distance of 1.432 Å and an $\angle \text{OSO}$ of 119.53° , while I_a and I_c lead to SO, 1.435 Å, and $\angle \text{OSO}$, 119.13° . One wonders about the point of reporting a value for the SO distance of 1.4321 Å.

Sulfamic acid (55, 56) has a crystal structure suggesting a *zwitterion* structure— $\text{H}_3\text{N}^+\text{SO}_3^-$ —for the molecule in view of the large difference between the SN distance (1.73 Å) and the SO distances (1.48 Å). New infrared data by Ketelaar & Veddar (57) on KHF_2 support the single minimum in the FHF potential energy function proposed by Pitzer & Westrum (58) from heat capacity data. The square pyramidal configuration in BrF_5 is favored over the trigonal bipyramid by observation of the Raman spectrum from the liquid (59).

The configuration of the I_3 ion in tetramethyl ammonium penta iodide is interesting [Hach & Rundle (60)]. The ion is v-shaped with an angle of 94° . The atom at the apex is separated by 3.14 Å from its neighbors, each of which holds another iodine atom at 2.93 Å. The ion may be roughly described as an iodide ion holding two iodine molecules and is quite different from the square ICl_4 ion observed by Mooney (61).

The infrared and visible spectrum of $\text{Fe}_3(\text{CO})_{12}$ leads to a model of D_{3d} symmetry with only two carbon monoxide molecules between adjacent iron atoms rather than three as occurs in $\text{Fe}_2(\text{CO})_9$ [Sheline (89)].

Organic compounds.—The structure of methyl alcohol has been worked out with more certainty by Burkhard & Dennison (62) with the aid of microwave data (63, 64) recently extended by Hughes, Good & Coles (65). For the purpose of predicting the microwave spectrum the molecule is represented by a rigid hydroxyl and a rigid methyl group experiencing a relative rotation hindered by the potential function, $V = \frac{1}{2}H(1 - \cos 3x)$. H is estimated from the earlier microwave data to be 1086 cal. per mole. Energy levels calculated from solutions of the Schroedinger equation for the molecule were used to predict the microwave spectrum which was in generally good agreement with the observed spectrum. The molecular constants combined with

assumed values for CH (1.093 Å), \angle HCH ($109^{\circ}28'$) and OH (0.958 Å) lead to a CO distance of 1.421 Å, an \angle COH of $110^{\circ}15'$, and the very interesting conclusion that the threefold axis of the methyl group does not pass through the oxygen atom but at a distance of 0.084 Å from the oxygen in the direction of the hydrogen atom.

Ethane has been investigated by Hedberg & Schomaker (11), who combined their electron diffraction data with the spectroscopic data of Smith (66). They report the CC bond length at 1.533 Å, the CH bond at 1.110 Å, and the \angle HCH at 108.5° with uncertainties of about 0.01 Å in the distances; and conclude that CC is not greater than 1.54 Å [Compare Herzberg's value (67) of 1.57 Å based in part on an assumed value for CH of 1.093 Å], that the CH bond is longer than in methane and the \angle HCH is smaller than the regular tetrahedral value. The last two conclusions are important since the moments of inertia in many methyl compounds have been interpreted with the assumption of methane parameters for the methyl group (cf. methyl alcohol above).

New infrared data by Herzberg, Jones & Leitch (68) for two species of methyl acetylene support the idea that methyl groups do not always have the methane parameters. Assuming the bond distances of acetylene (CC at 1.207 Å and CH at 1.059 Å) and the CH distance of methane, 1.093 Å, the authors use the two observed moments of inertia to obtain a CC value of 1.461 ± 0.006 Å and a \angle HCH value of $108^{\circ}6' \pm 1^{\circ}$, the latter being smaller than in methane.

A particularly good example of the combination of electron diffraction and microwave data is given by Shoolery *et al.* (32) for trifluoromethyl acetylene, whose microwave spectrum has also been studied by Anderson and co-workers (69). The first authors examined four isotopic species to obtain values for CH (1.056 ± 0.005 Å) and CC triple bond (1.201 ± 0.002 Å) from microwave data alone. Using these values in interpreting the diffraction data they further report the CC single bond at 1.464 ± 0.02 Å, the CF bond at 1.335 ± 0.01 Å and the \angle FCF at $107.5 \pm 1^{\circ}$. Of particular interest is the configuration of the CF_3 group, since this, the most reliable result to date, clearly shows a bond angle smaller than 109.5° .

Cochran (70) has made a very careful study of the electron distribution in adenine hydrochloride hemihydrate, whose crystal structure was determined by Broomhead (71, 72). Cochran's treatment of the Geiger counter data on x-ray intensities from two hundred fifty planes of the (h0l) zone is notable for achieving a value of only 0.061 for the reliability factor, R defined in terms of observed and calculated structure factors: $R = \Sigma |F_o - F_c| \div \Sigma |F_o|$. This was aided by considering anisotropic thermal vibrations of the nonhydrogen atoms. His careful calculations of standard deviations in the electron density function, in the atomic positions, and in the interatomic distances give his results a precise meaning rarely found in the two-dimensional electron density projections calculated from x-ray data. The bond

lengths involving carbon and nitrogen atoms have standard deviations not exceeding 0.01 Å. In the six-membered ring (Fig. 1) the bond lengths in order beginning with the 1, 2 positions are 1.37, 1.30, 1.36, 1.37, 1.40, 1.38 Å. In the five-membered ring the values are: C₄N₉, 1.36 Å; N₉C₈, 1.33 Å; C₈N₇, 1.35 Å; N₇C₅, 1.37 Å. The distance C₆N₁₀ is 1.30 Å. These lengths compared with single bond values of 1.54 Å for CC and 1.47 Å for CN and with double bond values of 1.34 Å and 1.28 Å, respectively, show a high degree of double bond character in all bond positions. It is noted that resonance among the

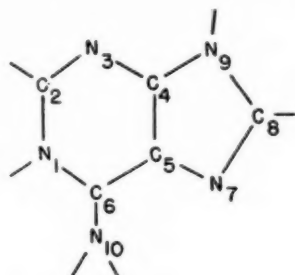


FIG. 1. Adenine ring system.

four unexcited bond structures consistent with the hydrogen positions indicated in Figure 1 will not account for the observed distances; for example, the bonds in the 8, 9, and 5, 7 positions appear as single bonds in all four structures. One of the interesting features of Cochran's investigation is the distinction between possible tautomers by determining definite locations for the hydrogen atoms.

Allen & Sutton (73) report on acetyl fluoride, chloride, bromide, and iodide from electron diffraction data covering ranges in s from 12.9 in the iodide to 17.8 in the chloride. Their values for the CX distances compared with the microwave values for the methyl halides tabulated in the 1951 *Review of Physical Chemistry* (2) show increases in the acetyl chloride, bromide, and iodide amounting to 2.2 per cent, 3.1 per cent and 3.3 per cent. Mackle & Sutton report electron diffraction results on carbon suboxide (74) and acraldehyde and crotonaldehyde (75); all bond distances have the expected values within the experimental uncertainty of ± 0.03 Å.

Microwave data on three isotopic species of ethylene oxide and of ethylene sulfide show three-membered rings with CC distances of 1.422 Å and 1.492 Å [Cunningham *et al.* (76)]. The decrease below 1.54 Å is ascribed to the directing of the bond orbitals on the carbon atoms at an angle to the line joining the two atoms. The other bond lengths have expected values, as do those in methyl mercaptan, whose microwave data are reported by Shaw & Windle (77). Sirvetz (78) assigns moments of inertia to furane in reasonable

agreement with values calculated from electron diffraction data (79). Nortri-cyclene, C_7H_{10} , shows an infrared spectrum from the solid and gas and a Raman spectrum from the liquid supporting the model with C_{3v} symmetry having three five-membered rings and one three-membered ring [Lippincott (80)].

X-ray crystal structure investigations affording intramolecular distances with uncertainties of about 0.05 Å or less include octachlorocyclobutane, showing a puckered four-membered ring with long CC bonds of 1.59 Å and CCl of 1.74 Å [Owen & Hoard (81)]. Marsh & McCullough (82) find SeC bonds in 1,4-diselenane 2 per cent longer than the value, 1.96 Å, in selenanthrene (83) and 3 per cent longer than 1.94 Å observed in the di-*p*-tolyl-selenium dihalides (84). Acetoxime, $(CH_3)_2CNOH$, forms a trimeric ring with CN bonds of 1.29 Å and NO bonds of 1.36 Å [Bierlein & Lingafelter (85)]. Brown (86) finds that *p*-aminophenol has a CO distance of 1.47 Å, considerably longer than the value 1.36 Å observed for CO in resorcinol (87). Tetramethyl pyrazine [Cromer, Ihde & Ritter (88)] has CC bonds of 1.44 Å in the aromatic ring, longer than the benzene value, 1.39 Å.

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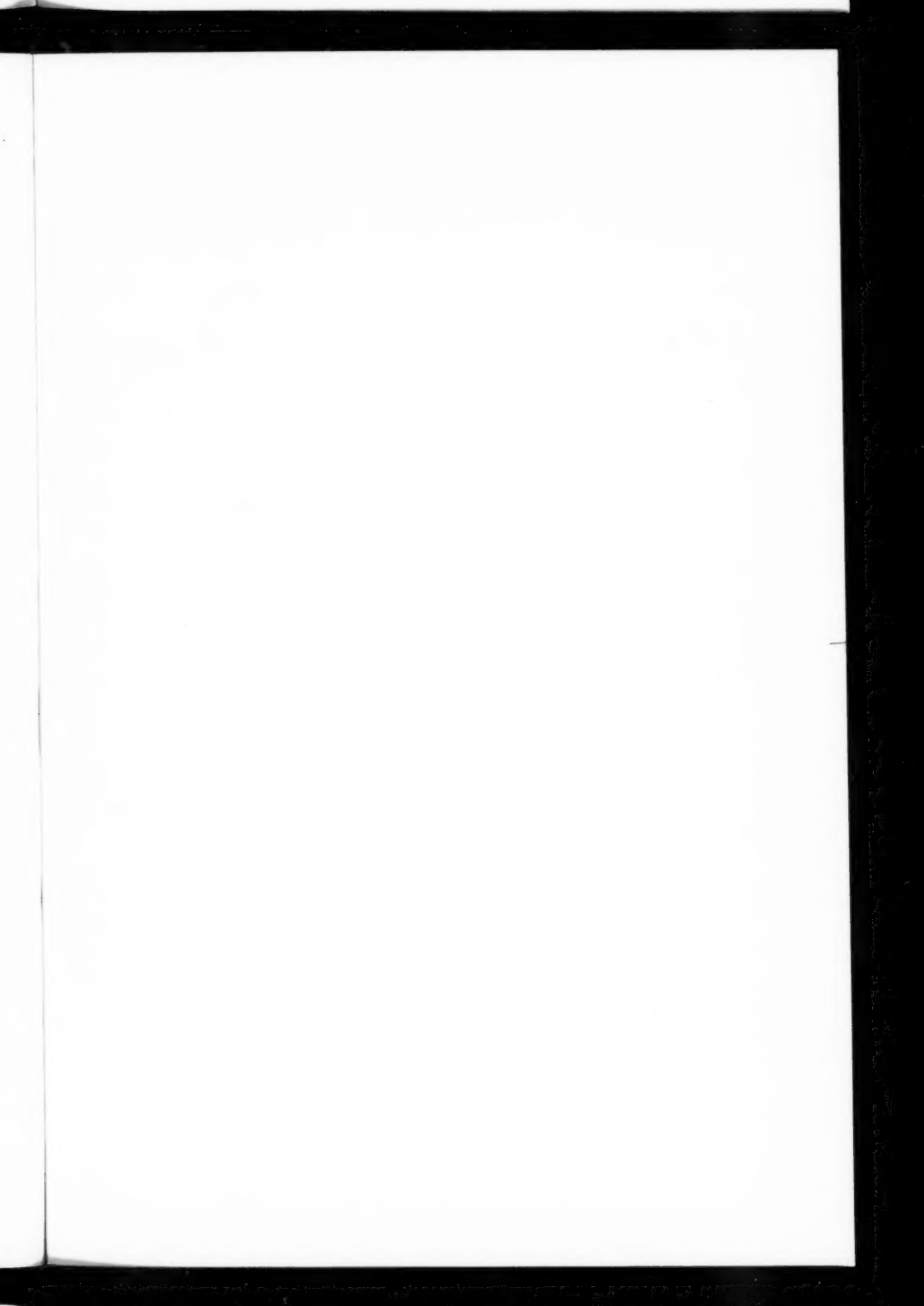
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